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Supporting Information

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A Highly Active and Recyclable Catalytic System for CO_2/(Propylene Oxide) Copolymerization

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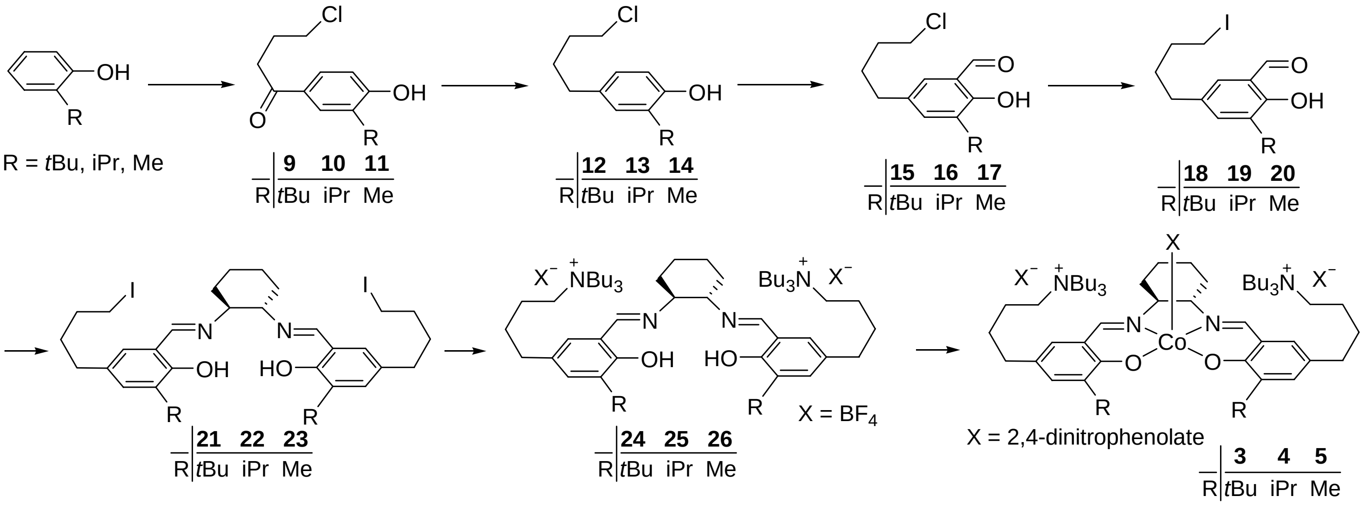
Supporting Information

General Remarks. All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. THF and C_6D_6 were distilled from benzophenone ketyl. Ethanol was dried by a method in the literature, using sodium and diethyl phthalate.[1] CH_3CN, CH_2Cl_2, and $CDCl_3$ were dried by stirring over CaH_2, and they were subsequently vacuum-transferred to reservoirs. The CO_2 gas (99.999%) was dried by storing it in a column of molecular sieves 3A at 30 bar. Propylene oxide (PO) was dried by stirring over CaH_2 for several days, and it was vacuum-transferred to a reservoir. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury Plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Gel permeation chromatograms (GPC) were obtained at room temperature in THF using Waters Millennium with polystyrene standards. The 1,7-dichloro-4-hepatanone,[2] 4-bromo-2-*tert*-butylphenol,[3] 4-bromo-2-isopropylphenol,[4] and 4-bromo-2-methylphenol[5] were prepared according to existing literature methods.



Synthesis of 9: A solution of 2-*tert*-butylphenol (1.50 g, 9.98 mmol) in CH_2Cl_2 (10 mL) was cooled to -

78 °C, and 4-chlorobutyryl chloride (1.41 g, 9.98 mmol) was added under a N_2 atmosphere. $AlCl_3$ (1.29 g, 9.68 mmol) was added to the reaction pot in small portions. The reaction mixture was stirred for 1 hour at -78°C, warmed to room temperature, and quenched by carefully and successively adding an ice and concentrated aqueous HCl solution (5 mL). The compound was extracted using CH_2Cl_2 (2 × 20 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v; 10:1). The product was obtained as a grey solid. The yields was 2.00 g (79%). M.p.: 121°C. IR (KBr): 3510 (OH), 1690 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.99 (d, *J* = 2.0 Hz, 1H, *m*-H), 7.76 (dd, *J* = 8.4, 2.0 Hz, 1H, *m*-H), 6.81 (d, *J* = 8.4 Hz, 1H, *o*-H), 6.70 (s, 1H, OH), 3.69 (t, *J* = 6.4 Hz, 2H, CH_2Cl), 3.17 (t, *J* = 7.2 Hz, 2H, CH_2CO), 2.25 (quintet, *J* = 6.0 Hz, 2H, CH_2), 1.45 (s, 9H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 198.83, 159.54, 136.28, 128.93, 128.16, 127.78, 116.27, 44.84, 34.97, 34.83, 29.38, 27.26 ppm. Anal. Calc. ($C_{14}H_{19}ClO_2$): C, 66.01; H, 7.52 %. Found: C, 66.18; H, 7.72 %.

Synthesis of 10: This compound was synthesized using the same conditions and procedure as those for **9**, starting with 2-isopropylphenol. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 7:1). A light yellow solid was obtained in 63% yield. M.p.: 78°C. IR (KBr): 3418 (OH), 1698 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.91 (d, *J* = 2.0 Hz, 1H, *m*-H), 7.50 (dd, *J* = 8.4, 2.0 Hz, 1H, *m*-H), 6.86 (d, *J* = 8.4 Hz, 1H, *o*-H), 6.62 (s, 1H, OH), 3.69 (t, *J* = 6.4 Hz, 2H, CH_2Cl), 3.29 (septet, *J* = 6.8 Hz, 1H, iPr-CH), 3.18 (t, *J* = 7.2 Hz, 2H, CH_2CO), 2.25 (quintet, *J* = 6.4 Hz, 2H, CH_2), 1.30 (d, *J* = 6.8 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 198.77, 158.00, 134.87, 129.50, 127.87, 127.17, 115.06, 44.81, 35.06, 27.29, 27.14, 22.44 ppm. Anal. Calc. ($C_{13}H_{17}ClO_2$): C, 64.86; H, 7.12 %. Found: C, 64.98; H, 7.15 %.

Synthesis of 11: To a flask containing $AlCl_3$ (1.85 g, 13.9 mmol) and 4-chlorobutyryl chloride (1.30 g, 9.25 mmol) in CH_2Cl_2 (10 mL), *o*-cresol (1.00 g, 9.25 mmol) was added at -20 °C over a period of 30 minutes under a N_2 atmosphere. The suspension was stirred for 3 hours, and quenched by careful addition of aqueous HCl (2 N). The solution was then extracted using CH_2Cl_2 (2 × 20 mL). The collected organic phase was dried over anhydrous $MgSO_4$, and all volatiles were removed with a rotary evaporator. Some of the desired products were further acylated on OH groups, which were hydrolyzed. The crude product was dissolved in methanol (10 mL), and $NaHCO_3$ (2.33 g, 27.8 mmol) was added. The resulting suspension was stirred at room temperature for two days. The solution was filtered over Celite, and the solvent was removed to give an oily residue, which was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 7:1). The product was obtained as an off-white solid. The yield was 1.10 g (58%). M.p.: 99°C. IR (KBr): 3420 (OH), 1706 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.82 (s, 1H, *m*-H), 7.77 (dd, *J* = 8.0, 2.0 Hz, 1H, *m*-H), 6.90 (s, 1H, OH), 6.88 (s, 1H, *o*-H), 3.68 (t, *J* = 6.4 Hz, 2H,

CH_2Cl), 3.17 (t, *J* = 6.4 Hz, 2H, CH_2CO), 2.32 (s, 3H, CH_3), 2.24 (quintet, *J* = 6.4 Hz, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 198.81, 159.04, 131.56, 129.13, 128.17, 124.37, 114.71, 44.79, 35.10, 27.17, 16.00 ppm. Anal. Calc. ($C_{11}H_{13}ClO_2$): C, 62.12; H, 6.16 %. Found: C, 62.33; H, 6.02 %.

Synthesis 12: This compound was synthesized using the same conditions and procedure as those for **14**, starting with **9**. A light yellow oil was obtained in quantitative yield. IR (KBr): 3531 (OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.08 (d, *J* = 2.4 Hz, 1H, *m*-H), 6.90 (dd, *J* = 8.0, 2.4 Hz, 1H, *m*-H), 6.62 (d, *J* = 8 Hz, 1H, *o*-H), 5.00 (s, 1H, OH), 3.59 (t, *J* = 6.4 Hz, 2H, CH_2Cl), 2.60 (t, *J* = 7.2 Hz, 2H, benzyl-CH_2), 1.90-1.72 (m, 4H, CH_2CH_2), 1.45 (s, 9H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.17, 135.72, 133.40, 126.92, 126.29, 115.25, 45.06, 34.65, 34.55, 32.27, 29.68, 28.99 ppm. HRMS (FAB): *m/z* calcd ($[M]^+$ $C_{14}H_{21}ClO$) 240.1281, found 240.1285.

Synthesis of 13: This compound was synthesized using the same conditions and procedure as those for **14**, starting with **10**. A light yellow oil was obtained in quantitative yield. IR (KBr): 3402 (OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.00 (d, *J* = 7.6 Hz, 1H, *m*-H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H, *m*-H), 6.68 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.73 (s, 1H, OH), 3.58 (t, *J* = 6.8 Hz, 2H, CH_2Cl), 3.22 (septet, *J* = 6.8 Hz, 1H, iPr-CH), 2.60 (t, *J* = 6.8 Hz, 2H, benzyl-CH_2), 1.88-1.72 (m, 4H, CH_2CH_2), 1.30 (d, *J* = 6.8 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.67, 134.15, 133.91, 126.16, 126.08, 115.03, 45.01, 34.56, 32.21, 28.94, 27.08, 22.70 ppm. HRMS (FAB): *m/z* calcd ($[M]^+$ $C_{13}H_{19}ClO$) 226.1124, found 226.1123.

Synthesis of 14: Compound **11** (1.80 g, 7.47 mmol) was dissolved in ethanol (7 mL), and then Pd on activated charcoal (10 w%-Pd, 64 mg) was added. The reaction mixture was stirred overnight at room temperature under an atmosphere of H_2 gas. The resulting solution was filtered over Celite, and the solvent was removed with a rotary evaporator to yield a light-brown oil that was pure enough to be used for the next reaction without further purification. Yields were quantitative. IR (KBr): 3523 (OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.96 (s, 1H, *m*-H), 6.90 (dd, *J* = 8.0, 2.0 Hz, 1H, *m*-H), 6.71 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.82 (s, 1H, OH), 3.58 (t, *J* = 6.4 Hz, 2H, CH_2Cl), 2.58 (t, *J* = 7.2 Hz, 2H, benzyl-CH_2), 2.27 (s, 3H, CH_3), 1.87-1.72 (m, 4H, CH_2CH_2) ppm. ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ 151.61, 133.84, 130.79, 126.62, 123.41, 114.62, 45.08, 34.23, 32.11, 28.93, 15.91 ppm. HRMS (FAB): *m/z* calcd ($[M]^+$ $C_{11}H_{15}ClO$) 198.0811, found 198.0811.

Synthesis of 15: This compound was synthesized using the same conditions and procedure as those for **17**, starting with **12**. A light yellow oil was obtained in quantitative yield. IR (KBr): 3480 (OH), 1718 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.64 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.34 (d, *J* = 2.0 Hz, 1H, *m*-H), 7.20 (d, *J* = 2.0 Hz, 1H, *m*-H), 3.59 (t, *J* = 6.8 Hz, 2H, CH_2Cl), 2.65 (t, *J* = 6.8 Hz, 2H, benzyl-CH_2), 1.90-1.76 (m, 4H, CH_2CH_2), 1.45 (s, 9H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.74 (CO), 159.27, 138.02, 134.44, 132.14, 130.61, 120.25, 44.85, 34.87, 34.35, 32.11, 29.32, 28.65 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{15}H_{22}ClO_2$) 269.1308, found 269.1304.

Synthesis of 16: This compound was synthesized using the same conditions and procedure as those for **17**, starting with **13**. A light yellow oil was obtained in quantitative yield. IR (KBr): 3531 (OH), 1732 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.22 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.28 (d, *J* = 1.6 Hz, 1H, *m*-H), 7.19 (d, *J* = 2.4 Hz, 1H, *m*-H), 3.59 (t, *J* = 6.0 Hz, 2H, CH_2Cl), 3.37 (septet, *J* = 6.8 Hz, 1H, iPr-CH), 2.65 (t, *J* = 6.8 Hz, 2H, benzyl-CH_2), 1.88-1.77 (m, 4H, CH_2CH_2), 1.27 (d, *J* = 6.8 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.52(CO), 157.32, 136.88, 133.88, 132.67, 130.09, 119.78, 44.87, 34.26, 32.07, 28.66, 26.38, 22.39 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{14}H_{20}ClO_2$) 255.1152, found 255.1151.

Synthesis of 17:[6] Compound **14** (1.50 g, 7.55 mmol) was dissolved in anhydrous THF (65 mL). Paraformaldehyde (0.906 g, 30.2 mmol), triethylamine (3.21 g, 31.7 mmol), and magnesium chloride (2.88 g, 30.2 mmol) were added under a N_2 atmosphere. The reaction mixture was heated to reflux for 4 hours and cooled to room temperature, after which the solvent was removed with a rotary evaporator. After water (75 mL) was added to the residue, the product was extracted using ethyl acetate (3 × 40 mL). The collected organic phase was dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to yield a residue that was pure enough to be used for the next reaction without further purification. Yields were quantitative. IR (KBr): 3493 (OH), 1716 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.11 (s, 1H, OH), 9.84 (s, 1H, CHO), 7.23 (d, *J* = 2.4 Hz, 1H, *m*-H), 7.18 (d, *J* = 2.4 Hz, 1H, *m*-H), 3.58 (t, *J* = 6.4 Hz, 2H, CH_2Cl), 2.62 (t, *J* = 6.8 Hz, 2H, benzyl-CH_2), 2.27 (s, 3H, CH_3), 1.87-1.76 (m, 4H, CH_2CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.31(CO), 158.02, 138.07, 132.49, 130.16, 126.58, 119.60, 44.83, 33.97, 32.00, 28.61, 15.15 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{12}H_{16}ClO_2$) 227.0839, found 227.0834.

Synthesis of 18: This compound was synthesized using the same conditions and procedure as those for **20**, starting with **15**. A light yellow oil was obtained in quantitative yield. IR (KBr): 3488 (OH), 1722 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.64 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.33(d, *J* = 2.0 Hz, 1H, *m*-H), 7.19 (d, *J* = 2.0 Hz, 1H, *m*-H), 3.24 (t, *J* = 7.2 Hz, 2H, CH_2I), 2.63 (t, *J* = 7.2 Hz, 2H, benzyl-CH_2), 1.89 (quintet, *J* = 7.2 Hz, 2H, CH_2), 1.75 (quintet, *J* = 7.2 Hz, 2H, CH_2), 1.44 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.74(CO), 159.27, 138.02, 134.44, 132.14, 130.61, 120.25, 44.85, 34.87, 34.35, 32.11, 29.32, 28.65 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{15}H_{22}IO_2$) 361.0665, found 361.0662.

Synthesis of 19: This compound was synthesized using the same conditions and procedure as those for **20**, starting with **16**. A light yellow oil was obtained in quantitative yield. IR (KBr): 3518 (OH), 1728 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.22 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.27 (d, *J* = 2.4 Hz, 1H, *m*-H), 7.18 (d, *J* = 2.4 Hz, 1H, *m*-H), 3.36 (septet, *J* = 6.8 Hz, 1H, iPr-CH), 3.23 (t, *J* = 6.4 Hz, 2H, CH_2I), 2.63 (t, *J* = 7.6 Hz, 2H, benzyl-CH_2), 1.88 (quintet, *J* = 7.2 Hz, 2H, CH_2), 1.75 (quintet, *J* = 7.2 Hz, 2H, CH_2), 1.26 (d, *J* = 7.2 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.51(CO), 157.28, 136.83, 133.86, 132.56, 130.07, 119.72, 33.87, 32.83, 32.20, 26.35, 22.38, 6.84 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{14}H_{20}IO_2$) 347.0508, found 347.0512.

Synthesis of 20: Compound **17** (0.56 g, 2.47 mmol) was dissolved in CH_3CN (5 mL) and NaI (3.16 g, 21.1 mmol) was added. The resulting mixture was stirred at 80°C for 20 hours. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The product was extracted using CH_2Cl_2 (3 × 10 mL). After the combined organic phase was dried over anhydrous $MgSO_4$, all volatiles were removed with a rotary evaporator to yield a yellow oil that was pure enough to be used for the next reaction without further purification. Yields were quantitative. IR (KBr): 3506 (OH), 1718 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.12 (s, 1H, OH), 9.84 (s, 1H, CHO), 7.22 (d, *J* = 2.4 Hz, 1H, *m*-H), 7.18 (d, *J* = 2.4 Hz, 1H, *m*-H), 3.22 (t, *J* = 7.2 Hz, 2H, CH_2I), 2.61 (t, *J* = 7.2 Hz, 2H, benzyl-CH_2), 2.27 (s, 3H, CH_3), 1.87 (quintet, *J* = 7.2 Hz, 2H, CH_2), 1.74 (quintet, *J* = 7.2 Hz, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.36(CO), 158.02, 138.09, 132.42, 130.18, 126.59, 119.55, 33.63, 32.78, 32.20, 15.21, 6.84 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{12}H_{16}IO_2$) 319.0195, found 319.0194.

Synthesis of 21: This compound was synthesized using the same conditions and procedure as those for **23**, starting with **18**. A light yellow glassy solid was obtained in 88% yield. IR (KBr): 3438 (OH), 1652 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.71 (s, 2H, OH), 8.27 (s, 2H, N=CH), 7.05 (s, 2H, *m*-H), 6.81 (s, 2H, *m*-H), 3.35-3.32 (m, 2H, cyclohexyl-CH), 3.19 (t, *J* = 6.8 Hz, 4H, -CH_2I), 2.51 (t, *J* = 7.2 Hz, 4H, benzyl-CH_2), 2.00-1.90 (m, 4H, cyclohexyl-CH_2), 1.82 (quintet, *J* = 7.2 Hz, 4H, CH_2), 1.66 (quintet, *J* = 7.2 Hz, 4H, CH_2), 1.55-1.45 (m, 4H, cyclohexyl-CH_2), 1.44 (s, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.21, 158.16, 136.71, 130.41, 129.38, 128.82, 118.17, 72.34, 34.80, 34.08, 33.22, 32.98, 32.40, 29.47, 24.40, 7.12 ppm. Anal. Calc. ($C_{36}H_{52}I_2N_2O_2$): C, 54.14; H, 6.56; N, 3.51 %. Found: C, 54.40; H, 6.32; N, 3.23 %.

Synthesis of 22: This compound was synthesized using the same conditions and procedure as those for **23**, starting with **19**. A light yellow solid was obtained in 93% yield. During the reaction, the product was deposited as a solid, which was collected and washed with ethanol. IR (KBr): 3443 (OH), 1641 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.53 (s, 2H, OH), 8.27 (s, 2H, N=CH), 7.01 (d, *J* = 1.6 Hz, 2H, *m*-H), 6.82 (d, *J* = 1.6 Hz, 2H, *m*-H), 3.38-3.30 (m, 4H, cyclohexyl-CH and iPr-CH), 3.19 (t, *J* = 7.2 Hz, 4H, CH_2I), 2.53 (t, *J* = 8.0 Hz, 4H, benzyl-CH_2), 1.95-1.88 (m, 4H, cyclohexyl-CH_2), 1.83 (quintet, *J* = 7.2 Hz, 4H, CH_2), 1.67 (quintet, *J* = 7.2 Hz, 4H, CH_2), 1.51-1.46 (m, 4H, cyclohexyl-CH_2), 1.26 (d, *J* = 4.8 Hz, 6H, iPr-CH_3), 1.24 (d, *J* = 4.8 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.71, 156.28, 135.66, 131.09, 128.75, 128.18, 117.65, 72.58, 33.99, 33.29, 32.91, 32.40, 26.44, 24.29, 22.62, 7.10 ppm. Anal. Calc. ($C_{34}H_{48}I_2N_2O_2$): C, 53.00; H, 6.28; N, 3.64 %. Found: C, 53.38; H, 6.40; N, 3.77 %.

Synthesis of 23: Compound **20** (0.260 g, 0.820 mmol) and (±)-*trans*-1,2-diaminocyclohexane (47 mg, 0.41 mmol) were weighed into a vial inside a glove box, and then dried ethanol (2 mL) was added. The reaction mixture was stirred overnight at room temperature. The reaction deposited a light-yellow oil. The solution phase was decanted off, and the deposited oil was evacuated under vacuum. A glassy solid was obtained with 90% yield (0.260 g). IR (KBr): 3421 (OH), 1633 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 13.43 (s, 2H, OH), 8.24 (s, 2H, N=CH), 6.95 (d, *J* = 2.0 Hz, 2H, *m*-H), 6.81 (d, *J* = 2.0 Hz, 2H, *m*-H), 3.33-3.31 (m, 2H, cyclohexyl-CH), 3.18 (t, *J* = 7.6 Hz, 4H, CH_2I), 2.50 (t, *J* = 7.2 Hz, 4H, benzyl-CH_2), 2.24 (s, 6H, CH_3), 1.94-1.85 (m, 4H, cyclohexyl-CH_2), 1.80 (quintet, *J* = 7.2 Hz, 4H, CH_2), 1.66 (quintet, *J* = 7.2 Hz, 4H, CH_2), 1.51-1.46 (m, 4H, cyclohexyl-CH_2) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 164.44, 157.12, 133.21, 130.98, 128.32, 125.32, 117.45, 72.66, 33.71, 33.27, 32.82, 32.36, 24.25, 15.62, 7.11 ppm. Anal. Calc. ($C_{30}H_{40}I_2N_2O_2$): C, 50.43; H, 5.64; N, 3.92 %. Found: C, 50.39; H, 5.73; N, 3.63 %.

Synthesis of 24: This compound was synthesized using the same conditions and procedure as those for **26**, starting with **21**. The product was purified by column chromatography on silica gel, eluting with EtOH and CH_2Cl_2 (v/v, 1:5). A yellow solid was obtained in 86% yield. IR (KBr): 3478 (OH), 1638 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.23 (s, 2H, N=CH), 7.04 (d, *J* = 2.0 Hz, 2H, *m*-H), 6.79 (d, *J* = 2.0 Hz, 2H, *m*-H), 3.36-3.28 (m, 2H, cyclohexyl-CH), 3.20-3.06 (m, 16H, NCH_2), 2.53 (t, *J* = 6.4 Hz, 4H, benzyl-CH_2), 2.02-1.94 (m, 2H, cyclohexyl-CH_2), 1.92-1.86 (m, 2H, cyclohexyl-CH_2), 1.76-1.66 (m, 4H, cyclohexyl-CH_2), 1.64-1.29 (m, 32H, CH_2), 1.40 (s, 18H, CH_3), 0.90 (t, *J* = 7.2 Hz, 18H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 165.25, 158.32, 136.76, 129.56, 129.22, 128.97, 118.19, 71.97, 58.28, 34.73, 34.06, 32.94, 29.46, 27.81, 24.22, 23.66, 21.00, 19.88, 19.53, 13.52 ppm. Anal. Calc. ($C_{60}H_{106}B_2F_8N_4O_2$): C, 66.17; H, 9.81; N, 5.14 %. Found: C, 66.45; H, 9.53; N, 4.92 %.

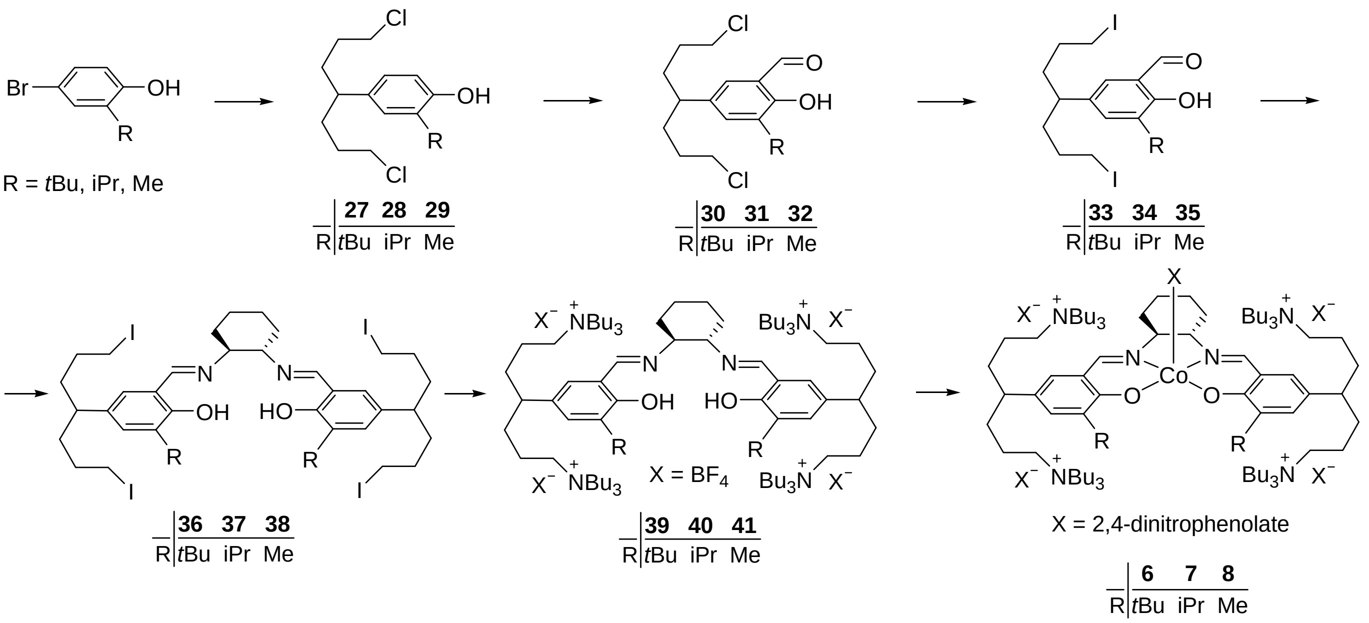
Synthesis of 25: This compound was synthesized using the same conditions and procedure as those for **26**, starting with **22**. The product was purified by column chromatography on silica gel, eluting with EtOH and CH_2Cl_2 (v/v, 1:5). A yellow solid was obtained in 85% yield. IR (KBr): 3433 (OH), 1654 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.24 (s, 2H, N=CH), 7.02 (d, *J* = 1.6 Hz, 2H, *m*-H), 6.80 (d, *J* = 1.6 Hz, 2H, *m*-H), 3.36-3.26 (4H, cyclohexyl-CH and iPr-CH), 3.20-3.06 (m, 16H, NCH_2), 2.55 (t, *J* = 6.8 Hz, 4H, benzyl-CH_2), 2.02-1.92 (m, 2H, cyclohexyl-CH_2), 1.90-1.84 (m, 2H, cyclohexyl-CH_2), 1.80-1.70 (m, 4H, cyclohexyl-CH_2), 1.66-1.44 (m, 24H, CH_2), 1.39-1.27 (m, 8H, CH_2), 1.23 (d, *J* = 5.2 Hz, 6H, iPr-CH_3**)**, 1.21 (d, *J* = 5.2 Hz, 6H, iPr-CH_3**)**, 0.92 (t, *J* = 7.6 Hz, 18H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 164.91, 156.53, 135.77, 130.28, 128.81, 128.39, 117.67, 72.18, 58.31, 33.99, 32.96, 27.85, 26.51, 24.15, 23.68, 22.65, 22.52, 20.99, 19.55, 13.54 ppm. Anal. Calc. ($C_{58}H_{102}B_2F_8N_4O_2$): C, 65.65; H, 9.69; N, 5.28 %. Found: C, 65.83; H, 9.77; N, 5.01 %.

Synthesis of 26: Compound **23** (0.292 g, 0.410 mmol) and tributylamine (0.303 g, 1.64 mmol) were weighed into a one-neck flask, and CH_3CN (5 mL) was added. After the flask was connected with a reflux condenser, the solution was refluxed for 2 days under a N_2 atmosphere. After the solution was cooled to room temperature, the solvent was removed under vacuum to give a residue, which was subsequently triturated in diethyl ether to give a light yellow powder in quantitative yield. To a flask containing the powder, $AgBF_4$ (0.160 g, 0.820 mmol) and EtOH (5 mL) were added. The solution was stirred overnight in the dark to generate AgI, which was filtered off inside a glove box. The solvent was removed under vacuum to give a yellow solid, which was purified by chromatography on a short pad of silica gel, eluting with EtOH and CH_2Cl_2 (v/v, 1:5). The yield was 0.47 g (88%). IR (KBr): 3418 (OH), 1656 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.20 (s, 2H, N=CH), 6.95 (d, *J* = 1.6 Hz, 2H, *m*-H), 6.79 (d, *J* = 1.6 Hz, 2H, *m*-H), 3.34-3.26 (m, 2H, cyclohexyl-CH), 3.20-3.00 (m, 16H, NCH_2), 2.52 (t, *J* = 6.4 Hz, 4H, benzyl-CH_2), 2.18 (s, 6H, CH_3), 1.96-1.82 (m, 4H, cyclohexyl-CH_2), 1.73-1.65 (m, 4H, cyclohexyl-CH_2), 1.60-1.44 (m, 24H, CH_2), 1.34-1.25 (m, 8H, CH_2), 0.88 (t, *J* = 7.6 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.52, 157.38, 133.26, 130.15, 128.51, 125.36, 117.52, 72.38, 58.30, 33.58, 33.10, 27.80, 24.16, 23.67, 20.75, 19.89, 19.54, 15.55, 13.55 ppm. Anal. Calc. ($C_{54}H_{94}B_2F_8N_4O_2$): C, 64.54; H, 9.43; N, 5.58 %. Found: C, 64.57; H, 9.48; N, 5.52 %.

Synthesis of 3: This compound was synthesized using the same conditions and procedure as those for **5**, starting with **24**. A brown powder was obtained in quantitative yield. The NMR signals are resonably sharp at room temperature. ^1H NMR (dmso-d_6, 38°C): δ 8.81 (br, 3H, $(NO_2)_2C_6H_3O$), 8.02 (br, 3H, $(NO_2)_2C_6H_3O$), 7.63 (s, 2H, CH=N), 7.28 (s, 2H, *m*-H), 7.21 (s, 2H, *m*-H), 6.56 (br, 3H, $(NO_2)_2C_6H_3O$), 3.58-3.68 (m, 2H, cyclohexyl-CH), 3.32-3.20 (m, 4H, NCH_2), 3.20-3.06 (m, 12H, NCH_2), 3.06-2.94 (m, 4H, cyclohexyl-CH), 2.64 (t, J = 7.6 Hz, 4H, CH_2), 2.06-1.96 (br, 2H, cyclohexyl-CH_2) 1.92-1.82 (br, 2H, cyclohexyl-CH_2), 1.72 (s, 18H, CH_3), 1.66-1.50 (m, 20H, CH_2), 1.40-1.24 (m, 12H, CH_2), 0.91 (t, *J* = 7.2 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR(dmso-d_6, 38 °C): δ 162.88, 161.40, 141.75, 131.09, 130.99, 127.60 (br, 2C, Salen-C and X-C), 126.15 (X-C), 124.53 (2C, X-C), 118.44, 68.61 (cyclohexyl-CH), 57.12 (CH_2NCH_2), 34.96 (*t*Bu-CH), 32.73 (benzyl-CH_2), 29.82 (*t*Bu-CH_3), 28.90 (cyclohexyl-CH_2), 27.44 (CH_2), 23.75 (cyclohexyl-CH_2), 22.58 (butyl-CH_2), 20.38 (CH_2), 18.70 (butyl-CH_2), 12.90 (butyl-CH_3) ppm. Two 2,4-dinitrophenolate signals at ~165 and ~137 ppm were missing due to broadening. Anal. Calc. ($C_{78}H_{113}CoN_{10}O_{17}\cdot 0.5NaBF_4$): C, 59.40; H, 7.23; N, 8.89 %. Found: C, 59.83; H, 7.22; N, 8.85 %. HRMS (FAB): m/z calcd ($[M-2\{(NO_2)_2C_6H_3O\}]^+$ $C_{66}H_{107}CoN_6O_7$) 1154.7533, found 1154.7539.

Synthesis of 4: This compound was synthesized using the same conditions and procedure as those for **5**, starting with **25**. A brown powder was obtained in quantitative yield. The NMR signals are sharp at room temperature. ^1H NMR (dmso-d_6, 70°C): δ 8.69 (br, 3H, $(NO_2)_2C_6H_3O$), 7.99 (br, 3H, $(NO_2)_2C_6H_3O$), 7.54 (s, 2H, N=CH), 7.25 (d, *J* = 2.0 Hz, 2H, *m*-H), 7.17 (d, *J* = 2.0 Hz, 2H, *m*-H), 6.69 (br, 3H, $(NO_2)_2C_6H_3O$), 4.09 (quintet, *J* = 6.8 Hz, 2H, iPr-CH), 3.84 (m, 2H, cyclohexyl-CH), 3.30-3.22 (m, 4H, NCH_2), 3.22-3.12 (m, 12H, NCH_2), 3.10-3.00 (m, 4H, cyclohexyl-CH_2), 2.71 (t, *J* = 7.2 Hz, 4H, benzyl-CH_2), 2.08-1.94 (m, 2H, cyclohexyl-CH_2) 1.92-1.82 (m, 2H, cyclohexyl-CH_2), 1.74-1.56 (m, 20H, CH_2), 1.45 (d, *J* = 6.8 Hz, 12H, iPr-CH_3), 1.33 (m, 12H, CH_2), 0.94 (t, *J* = 7.2 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR(dmso-d_6, 38 °C): δ 162.68 (br), 160.20, 140.58, 130.48, 130.32, 127.44 (br, 2C, Salen-C and X-C), 126.55 (X-C), 124.65 (2C, X-C), 117.57, 68.90 (cyclohexyl-CH), 57.26 (CH_2NCH_2), 32.95 (benzyl-CH_2), 28.97 (cyclohexyl-CH_2), 27.52 (CH_2), 27.42 (iPr-CH), 23.92 (cyclohexyl-CH_2), 23.13 (iPr-CH_3), 22.72 (butyl-CH_2), 22.24 (iPr-CH_3), 20.45 (CH_2), 18.83 (butyl-CH_2), 13.03 (butyl-CH_3) ppm. Two 2,4-dinitrophenolate signals at ~165 and ~137 ppm were missing due to broadening. Anal. Calc. ($C_{76}H_{109}CoN_{10}O_{17}\cdot 0.5NaBF_4$): C, 58.93; H, 7.10; N, 9.05 %. Found: C, 59.15; H, 7.07; N, 8.90 %. HRMS (FAB): m/z calcd ($[M-2\{(NO_2)_2C_6H_3O\}]^+$ $C_{64}H_{103}CoN_6O_7$) 1126.7220, found 1126.7228.

Synthesis of 5: Cobalt (II) acetate (38 mg, 0.22 mmol) and **26** (0.221 g, 0.220 mmol) were dissolved in ethanol (5 mL) inside a glovebox. Red solid precipitated immediately. After stirring for 2 hours at room temperature, the solvent was removed, and the residue was triturated in diethyl ether. The solid was dissolved in CH_2Cl_2 containing 2,4-dinitrophenol (48 mg, 0.22 mmol), and the resulting solution was stirred for 2 hours under an O_2 atmosphere. After sodium 2,4-dinitrophenolate (0.136 g, 0.660 mmol) was added, the reaction mixture was stirred overnight at room temperature. The solution was filtered over Celite, and the solvent was removed under vacuum to give a brown powder that was pure enough to be used for polymerization without further purification. Yields were quantitative. The NMR signals were broad at room temperature, but they became sharp after raising the temperature to 70°C. The CHN elemental analysis data deviated a little from the calculated values, but they were well in agreement with the structure containing additional 0.5 equivalent of $NaBF_4$. We presume that some $NaBF_4$ was extracted out into CH_2Cl_2 phase during the final salt exchange reaction. We also observed a characteristic BF_4 signal in the ^{19}F NMR. In the high resolution mass (FAB) study, we observed a signal corresponding to M-2[2,4-$(NO_2)_2C_6H_3O$]. A 2,4-$(NO_2)_2C_6H_3O$ anion was lost to give a positively charged species and the other 2,4-$(NO_2)_2C_6H_3O$ fragment may be lost as a radical to give a cobalt(II) species. ^1H NMR (dmso-d_6, 70°C): δ 8.62 (s, 3H, $(NO_2)_2C_6H_3O$), 8.33 (d, J = 6.8 Hz, 3H, $(NO_2)_2C_6H_3O$), 7.61 (s, 2H, N=CH), 7.23 (s, 2H, *m*-H), 7.15 (s, 2H, *m*-H), 6.62 (br, 3H, $(NO_2)_2C_6H_3O$), 3.80-3.70 (m, 2H, cyclohexyl-CH), 3.30-3.10 (m, 16H, NCH_2), 3.08-3.00 (m, 4H, cyclohexyl-CH_2), 2.68 (s, 6H, CH_3), 2.65-2.60 (m, 4H, benzyl-CH_2), 2.10-2.00 (m, 2H, cyclohexyl-CH_2), 1.95-1.80 (m, 2H, cyclohexyl-CH_2), 1.75-1.50 (m, 20H, CH_2), 1.40-1.25 (m, 12H, CH_2), 0.92 (t, *J* = 7.2 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR(dmso-d_6, 38 °C): δ 162.84 (br), 160.01, 134.43, 130.70, 130.05, 127.42 (br, 2C, Salen-C and X-C), 126.46 (br, X-C), 124.58 (2C, X-C), 116.99, 69.12 (cyclohexyl-CH), 57.34 (CH_2NCH_2), 32.66 (CH_2), 29.11 (cyclohexyl-CH_2), 27.46 (CH_2), 24.04 (cyclohexyl-CH_2), 22.82 (butyl-CH_2), 20.34 (CH_2), 18.93 (butyl-CH_2), 16.76 (CH_3), 13.14 (butyl-CH_3) ppm. Two 2,4-dinitrophenolate signals at ~165 and ~137 ppm were missing due to broadening. Anal. Calc. ($C_{72}H_{101}CoN_{10}O_{17}\cdot 0.5NaBF_4$): C, 57.94; H, 6.82; N, 9.39 %. Found: C, 57.91; H, 6.93; N, 9.27 %. HRMS (FAB): m/z calcd ($[M-2\{(NO_2)_2C_6H_3O\}]^+$ $C_{60}H_{95}CoN_6O_7$) 1070.6594, found 1070.6588.



Synthesis of 27: This compound was synthesized using the same conditions and procedure as those for **29**, starting with 4-bromo-2-*tert*-butylphenol. In this case, the resulting benzylic tertiary alcohol was not eliminated during the work-up and it was isolated in 82% yield by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 5:1). The hydrogenated compound was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 10:1). The hydrogenation yield was 83%. The compound was obtained as a colourless oil. IR (KBr): 3545 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ. 7.02 (d, *J* = 2.0 Hz, 1H, *m*-H), 6.84 (dd, *J* = 8.0, 2.0 Hz, 1H, *m*-H), 6.62 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.93 (s, 1H, OH), 3.49 (t, *J* = 5.6 Hz, 4H, CH_2Cl), 2.49 (quintet, *J* = 4.8 Hz, 1H, CH), 1.88-1.61 (m, 8H, CH_2), 1.45 (s, 9H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.36, 135.86, 135.82, 126.02, 125.21, 115.38, 45.26, 44.34, 34.56, 34.14, 30.66, 29.71 ppm. HRMS (FAB): *m/z* calcd ($[M]^+$ $C_{17}H_{26}Cl_2O$) 316.1361, found 316.1360.

Synthesis of 28: This compound was synthesized using the same conditions and procedure as those for **29**, starting with 4-bromo-2-isopropylphenol. In this case, the resulting benzylic tertiary alcohol was not eliminated during the work-up and it was isolated in 79% yield by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 5:1). The hydrogenated compound was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 10:1). The hydrogenation yield was 80%. The compound was obtained as a colorless oil. IR (KBr): 3562 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ. 6.94 (d, *J* = 2.0 Hz, 1H, *m*-H), 6.83 (dd, *J* = 8.0, 2.0 Hz, 1H, *m*-H), 6.69 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.73 (s, 1H, OH), 3.48 (t, *J* = 5.6 Hz, 4H, CH_2Cl), 3.21 (septet, *J* = 6.8 Hz, 1H, iPr-CH), 2.48 (quintet, *J* = 4.8 Hz, 1H, CH), 1.82-1.60 (m, 8H, CH_2), 1.28 (d, *J* = 6.8 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.86, 136.39, 134.21, 125.30, 125.12, 115.16, 45.27, 44.34, 34.17, 30.66, 27.17, 22.71 ppm. HRMS (FAB): *m/z* calcd ($[M]^+$ $C_{16}H_{24}OCl_2$) 302.1204, found 302.1206.

Synthesis of 29: 4-Bromo-2-methylphenol (10.0 g, 53.5 mmol) was added to a one-neck flask and combined with THF (450 mL). After the solution was cooled to -78°C, *tert*-BuLi (1.7 M in pentane, 160 g, 176 mmol) was added dropwise. After the solution was stirred for 2 hours at -78°C, a solution containing both 1,7-dichloro-4-heptanone (11.8 g, 64.2 mmol) and LiCl (2.72 g, 64.2 mmol) in THF (80 mL) was added dropwise using a syringe for 2 hours. After the solution was stirred for 2 hours at -78°C, aqueous saturated NH_4Cl solution (150 mL) was added to quench the reaction. The product was extracted using diethyl ether (3 × 100 ml). After the combined organic phase was dried over anhydrous $MgSO_4$, the solvent was removed with a rotary evaporator to give an oily residue. Some of the resulting benzylic tertiary alcohol was H_2O-eliminated, transformed to the corresponding alkene, and a mixture of the benzylic tertiary alcohol and its H_2O-eliminated alkene compound was obtained. The major side product of this reaction was 2-methylphenol, generated by protonation of the lithiated compound. It was not easy to separate out 2-methylphenol from the hydrogenated product or from the H_2O-eliminated alkene compound by column chromatography; therefore, the 2-methylphenol side product was eliminated by the following procedure: The oily residue was transferred into a separatory funnel, and then diethyl ether (80 mL) and aqueous KOH solution (22 w%, 40 mL) were added. The mixture was vigorously shaken to give three phases: an upper diethyl ether phase, a middle phase of potassium salt of the desired products, and a bottom aqueous phase containing potassium 2-methylphenolate. After the bottom layer was discarded, aqueous saturated NH_4Cl solution (30 mL) was added. The addition protonated the phenolate anions in the desired products to solubilize them in the diethyl ether phase. The ether phase was collected and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give an oily residue that was purified by column chromatography. The H_2O-eliminated alkene compound was obtained by eluting with hexane and ethyl acetate (v/v, 10:1), and the benzylic tertiary alcohol was obtained by eluting with hexane and ethyl acetate (v/v, 2:1). The two compounds were combined and dissolved in ethanol (40 mL). Pd on activated charcoal (10 w%, 420 mg) was added, and the solution was stirred overnight at room temperature under an atmosphere of H_2 gas. The solution was filtered over Celite, and the solvent was removed with a rotary evaporator to give a residue that was subsequently purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 10:1). The product was obtained as a colourless oil (7.27 g, 67%). IR (KBr): 3538 (OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ. 6.88 (d, *J* = 2.0 Hz, 1H, *m*-H), 6.82 (dd, *J* = 8.0, 2.0 Hz, 1H, *m*-H), 6.72 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.76 (s, 1H, OH), 3.49 (t, *J* = 6.8 Hz, 4H, CH_2Cl), 2.44 (quintet, *J* = 4.8 Hz, 1H, CH), 2.28 (s, 3H, CH_3), 1.82-1.60 (m, 8H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.89, 136.13, 129.79, 125.67, 123.66, 114.77, 45.24, 44.03, 34.17, 30.63, 16.04 ppm. HRMS (FAB): *m/z* calcd ($[M]^+$ $C_{14}H_{20}OCl_2$) 274.0891, found 274.0895.

Synthesis of 30: This compound was synthesized using the same conditions and procedure as those for **32**, starting with **27**. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 10:1). A colourless oil was obtained in 86% yield. IR (KBr): 3549 (OH), 1733 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.67 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.31 (d, *J* = 2.4 Hz, 1H, *m*-H), 7.16 (d, *J* = 2.4 Hz, 1H, *m*-H), 3.49 (t, *J* = 5.6 Hz, 4H, CH$_2$Cl), 2.56 (quintet, *J* = 5.2 Hz, 1H, CH), 1.88-1.59 (m, 8H, CH$_2$), 1.44 (s, 9H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 196.74, 159.50, 138.29, 134.59, 133.17, 129.91, 120.25, 45.02, 44.19, 34.91, 33.85, 30.51, 29.28 ppm. HRMS (FAB): *m/z* calcd ([M+H]$^+$ $C_{18}H_{27}Cl_2O_2$) 345.1388, found 345.1386.

Synthesis of 31: This compound was synthesized using the same conditions and procedure as those for **32**, starting with **28**. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 10:1). A light yellow oil was obtained in 94% yield. IR (KBr): 3558 (OH), 1721 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.22 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.22 (d, *J* = 2.0 Hz, 1H, *m*-H), 7.13 (d, *J* = 2.0 Hz, 1H, *m*-H), 3.48 (t, *J* = 6.4 Hz, 4H, CH$_2$Cl), 3.35 (septet, *J* = 6.8 Hz, 1H, iPr-CH), 2.58 (quintet, *J* = 5.2 Hz, 1H, CH), 1.86-1.56 (m, 8H, CH$_2$), 1.26 (d, *J* = 6.8 Hz, 6H, iPr-CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 197.02, 158.16, 137.80, 135.65, 133.14, 129.91, 120.36, 45.54, 44.72, 34.44, 31.05, 27.01, 22.90 ppm. HRMS (FAB): *m/z* calcd ([M+H]$^+$ $C_{17}H_{25}Cl_2O_2$) 331.1232, found 331.1234.

Synthesis of 32:[6] Compound **29** (7.27 g, 26.4 mmol) was dissolved in anhydrous THF (500 mL). Paraformaldehyde (3.17 g, 106 mmol), triethylamine (11.2 g, 111 mmol) and magnesium chloride (10.1 g, 106 mmol) were added under a N$_2$ atmosphere. The reaction mixture was heated to reflux for 5 hours and cooled to room temperature. The solvent was removed with a rotary evaporator. Water (150 mL) and CH$_2$Cl$_2$ (100 mL) were added to the residue, and the mixture was filtered over Celite. The organic phase was collected, and the aqueous phase was further extracted using CH$_2$Cl$_2$ (2 × 100 mL). The combined organic phase was dried over anhydrous MgSO$_4$. The solvent was removed with a rotary evaporator to give a residue that was subsequently purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 30:1). A light yellow oil was obtained in 76% yield (6.03 g). IR (KBr): 3544 (OH), 1729 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.14 (s, 1H, OH), 9.86 (s, 1H, CHO), 7.18 (d, *J* = 2.0 Hz, 1H, *m*-H), 7.15 (d, *J* = 2.0 Hz, 1H, *m*-H), 3.49 (t, *J* = 6.4 Hz, 4H, CH$_2$Cl), 2.53 (quintet, *J* = 4.0 Hz, 1H, CH), 2.28 (s, 3H, CH$_3$), 1.88-1.58 (m, 8H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 196.33, 158.37, 136.72, 135.00, 129.61, 127.05, 119.65, 45.01, 44.06, 33.99, 30.58, 15.37 ppm. HRMS (FAB): *m/z* calcd ([M+H]$^+$ $C_{15}H_{21}Cl_2O_2$) 303.0919, found 303.0919.

Synthesis of 33: This compound was synthesized using the same conditions and procedure as those for **35**, starting with **30**. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 15:1). A yellow oil was obtained in 87% yield. IR (KBr): 3540 (OH), 1731 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 11.67 (s, 1H, OH), 9.85 (s, 1H, CHO), 7.29 (d, *J* = 2.4 Hz, 1H, *m*-H), 7.13 (d, *J* = 2.4 Hz, 1H, *m*-H), 3.13 (m, 4H, CH$_2$I), 2.54 (quintet, *J* = 4.8 Hz, 1H, CH), 1.80-1.61 (m, 8H, CH$_2$), 1.43 (s, 9H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 196.75, 159.57, 138.37, 134.49, 133.10, 129.95, 120.21, 43.67, 37.37, 34.97, 31.25, 29.32, 7.22 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{18}H_{27}I_2O_2$) 529.0101, found 529.0101.

Synthesis of 34: This compound was synthesized using the same conditions and procedure as those for **35**, starting with **31**. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 15:1). A yellow oil was obtained in 81% yield. IR (KBr): 3553 (OH), 1727 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.28 (s, 1H, OH), 9.90 (s, 1H, CHO), 7.27 (d, *J* = 1.6 Hz, 1H, *m*-H), 7.17 (d, *J* = 1.6 Hz, 1H, *m*-H), 3.40 (septet, *J* = 7.2 Hz, 1H, iPr-CH), 3.18 (m, 4H, CH_2I), 2.61 (quintet, *J* = 4.4 Hz, 1H, CH), 1.88-1.60 (m, 8H, CH_2), 1.31 (d, *J* = 6.8 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.17, 157.31, 136.94, 134.70, 132.23, 129.09, 119.45, 43.28, 37.09, 30.92, 26.16, 22.09, 6.84 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{17}H_{25}I_2O_2$) 514.9944, found 514.9943.

Synthesis of 35: Compound **32** (5.24 g, 17.3 mmol) was dissolved in CH_3CN (20 mL) and NaI (25.9 g, 173 mmol) was added. After the resulting mixture was stirred at 80°C for 20 hours, it was cooled to room temperature. After water (100 mL) was added, the product was extracted using diethyl ether (3 × 50 mL). After the collected organic phase was dried over anhydrous $MgSO_4$, all volatiles were removed with a rotary evaporator to give a yellow oil that was subsequently purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v; 30:1). The yield was 89% (7.55 g). IR (KBr): 3528 (OH), 1723 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.12 (s, 1H, OH), 9.84 (s, 1H, CHO), 7.15 (d, *J* = 2.4 Hz, 1H, *m*-H), 7.12 (d, *J* = 2.4 Hz, 1H, *m*-H), 3.12 (t, *J* = 6.0 Hz, 4H, CH_2I), 2.51 (quintet, *J* = 4.8 Hz, 1H, CH), 2.26 (s, 3H, CH_3), 1.81-1.57 (m, 8H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.68, 158.71, 137.04, 135.26, 129.93, 127.39, 119.95, 43.82, 37.86, 31.66, 15.75, 7.40 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{15}H_{21}I_2O_2$) 486.9631, found 486.9626.

Synthesis of 36: This compound was synthesized using the same conditions and procedure as those for **38**, starting with **33**. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v; 10:1). A yellow solid was obtained in 88% yield. IR (KBr): 3452 (OH), 1644 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.72 (s, 2H, OH), 8.30 (s, 2H, N=CH), 7.00 (d, *J* = 2.0 Hz, 2H, *m*-H), 6.76 (d, *J* = 2.0 Hz, 2H, *m*-H), 3.37-3.35 (m, 2H, cyclohexyl-CH), 3.07 (t, *J* = 6.4 Hz, 4H, CH_2I), 2.42 (quintet, *J* = 4.0 Hz, 2H, CH), 1.98-1.86 (m, 4H, cyclohexyl-CH_2), 1.74-1.54 (m, 20H, cyclohexyl-CH_2 and CH_2), 1.41 (s, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.40, 158.84, 137.36, 133.30, 128.60, 128.34, 118.63, 72.54, 43.92, 37.87, 37.69, 35.22, 33.70, 31.65, 31.52, 29.81, 24.68, 8.03, 7.87 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{42}H_{63}O_2N_2I_4$) 1135.1069, found 1135.1074.

Synthesis of 37: This compound was synthesized using the same conditions and procedure as those for **38**, starting with **34**. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v; 10:1). A yellow solid was obtained in 76% yield. IR (KBr): 3486 (OH), 1649 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.51 (s, 2H, OH), 8.30 (s, 2H, N=CH), 6.94 (s, 2H, *m*-H), 6.78 (s, 2H, *m*-H), 3.40-3.20 (m, 4H, iPr-CH and cyclohexyl-CH), 3.07 (t, *J* = 5.2 Hz, 4H, CH_2I), 2.45 (quintet, *J* = 4.4 Hz, 2H, CH), 1.93-1.86 (m, 4H, cyclohexyl-CH_2), 1.80-1.48 (m, 20H, cyclohexyl-CH_2 and CH_2), 1.23 (d, *J* = 6.8 Hz, 6H, iPr-CH_3), 1.21 (d, *J* = 6.8 Hz, 6H, iPr-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.96, 156.99, 136.30, 133.97, 127.99, 127.74, 118.18, 72.85, 43.89, 37.88, 37.79, 33.80, 31.63, 31.53, 26.94, 24.60, 22.99, 22.96, 7.96, 7.84 ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{40}H_{59}O_2N_2I_4$) 1107.0756, found 1107.0748.

Synthesis of 38: Compound **35** (4.00 g, 8.23 mmol) and (±)-*trans*-1,2-diaminocyclohexane (0.470 g, 4.12 mmol) were weighed into a one-neck flask, and then CH_2Cl_2 (50 mL) and molecular sieves (1.20 g) were added. The solution was heated to 35°C for 2 days under a N_2 atmosphere. The resulting solution was filtered, and the solvent was removed under vacuum. The ^1H NMR spectrum indicated that the product was pure, and it was used in the next step without further purification (4.24 g, 98%). IR (KBr): 3423 (OH), 1653 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.43 (s, 2H, OH), 8.29 (s, 2H, CHO), 6.89 (d, *J* = 1.6 Hz, 2H, *m*-H), 6.79 (d, *J* = 1.6 Hz, 2H, *m*-H), 3.42-3.30 (m, 2H, cyclohexyl-CH), 3.08 (t, *J* = 6.4 Hz, 8H, CH_2I), 2.42 (quintet, *J* = 4.4 Hz, 2H, CH), 2.24 (s, 6H, CH_3), 2.02-1.84 (m, 4H, cyclohexyl-CH_2), 1.80-1.46 (m, 20H, cyclohexyl-CH_2 and CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.67, 157.67, 133.73, 132.29, 127.85, 125.82, 117.87, 72.86 (cyclohexyl-CH), 43.61 (benzyl-CH), 37.81 (CH_2), 33.58 (cyclohexyl-CH_2), 31.58 and 31.48 (I-CH_2CH_2), 24.47 (cyclohexyl-CH_2), 16.03 (CH_3), 7.65 and 7.56 (I-CH_2) ppm. Anal. Calc. ($C_{36}H_{50}I_4N_2O_2$): C, 41.16; H, 4.80; N, 2.67 %. Found: C, 41.30; H, 4.90; N, 2.81 %.

Synthesis of 39: This compound was synthesized using the same conditions and procedure as those for **41**, starting with **36**. The product was purified by column chromatography on a short pad of silica gel, eluting with EtOH and CH_2Cl_2 (v/v, 1:5). A light yellow solid was obtained in 87% yield. IR (KBr): 3459 (OH), 1648 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.91 (s, 2H, OH), 8.40 (s, 2H, CH=N), 7.04 (s, 4H, phenyl-H), 3.50-3.40 (m, 2H, cyclohexyl-CH), 3.35-2.95 (m, 32H, NCH_2), 2.63 (quintet, *J* = 6.8 Hz, 2H, CH), 1.95-1.80 (m, 4H, cyclohexyl-CH_2), 1.75-1.20 (m, 68H), 1.39 (s, 18H, CH_3), 0.90 (t, *J* = 7.2 Hz, 18H, CH_3), 0.80 (t, *J* = 7.6 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.33, 159.67, 138.26, 131.67, 129.32, 127.92, 119.01, 72.52 (cyclohexyl-CH), 58.68 (NCH_2), 58.45 (NCH_2), 41.73 (benzyl-CH), 35.45 (*t*Bu-CH), 34.06 (CH_2), 33.77 (CH_2), 33.07 (CH_2), 29.93 (*t*Bu-CH_3), 24.79 (cyclohexyl-CH_2), 24.14 and 24.02 (butyl-CH_2), 20.07 and 19.92 (butyl-CH_2), 19.47 (cyclohexyl-CH_2), 14.06 and 13.87 (butyl-CH_3) ppm. Anal. Calc. ($C_{90}H_{170}B_4F_{16}N_6O_2$): C, 63.01; H, 9.99; N, 4.90 %. Found: C, 63.32; H, 10.12; N, 4.81 %.

Synthesis of 40: This compound was synthesized using the same conditions and procedure as those for **41**, starting with **37**. The product was purified by column chromatography on a short pad of silica gel, eluting with EtOH and CH_2Cl_2 (v/v, 1:5). A light yellow solid was obtained in 96% yield. IR (KBr): 3472 (OH), 1642 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.68 (br s, 2H, OH), 8.39 (s, 2H, CH=N), 7.02 (s, 4H, *m*-

H), 3.46-3.38 (m, 2H, cyclohexyl-CH), 3.31 (quintet, *J* = 6.8 Hz, 2H, iPr-CH), 3.26-2.96 (m, 32H, NCH_2), 2.66 (quintet, *J* = 7.2 Hz, 2H, CH), 1.88-1.82 (m, 4H, cyclohexyl-CH_2), 1.76-1.40 (m, 52H), 1.37-1.19 (m, 28H, iPr-CH_3 and CH_2), 0.91 (t, *J* = 6.8 Hz, 18H, CH_3), 0.84 (t, *J* = 6.8 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.97, 157.91, 137.09, 132.47, 128.58, 127.71, 118.51, 72.76 (cyclohexyl-CH), 58.70 (NCH_2), 58.49 (NCH_2), 41.73 (-CH-), 33.96 (-CH_2-), 33.69 (-CH_2-), 33.04 (-CH_2-), 27.51 (iPr-CH), 24.71 (cyclohexyl-CH_2), 24.15 and 24.06 (butyl-CH_2), 23.06 (iPr-CH_3), 22.85 (iPr-CH_3), 20.09 and 19.95 (butyl-CH_2), 19.44 (cyclohexyl-CH_2), 14.08 and 13.93 (butyl-CH_3) ppm. Anal. Calc. ($C_{88}H_{166}B_4F_{16}N_6O_2$): C, 62.63; H, 9.92; N, 4.98 %. Found: C, 62.42; H, 9.97; N, 4.82 %.

Synthesis of 41: Compound **38** (4.07 g, 3.87 mmol) and tributylamine (5.75 g, 31.0 mmol) were weighed into a one-neck flask, and CH_3CN (40 mL) was added. The solution was refluxed for 2 days under a N_2 atmosphere. After the solution was cooled to room temperature, the solvent was removed under vacuum to give a residue that was subsequently triturated in diethyl ether to give a light yellow powder in 95% yield (6.61 g). To a flask containing the powder (0.200 g, 0.112 mmol), $AgBF_4$ (0.087 g, 0.446 mmol) and ethanol (6 mL) were added. The solution was stirred for a day in the dark. After the generated AgI was filtered off over Celite inside a glove box, the solvent was immediately removed under vacuum to give a residue that was redissolved in CH_2Cl_2 (~ 4 mL). The solution was filtered again over Celite, and the solvent was removed under vacuum to yield a yellow residue that was subsequently purified by column chromatography on a short pad of silica gel, eluting with EtOH and CH_2Cl_2 (v/v, 1:5). The yield was 0.146 mg (80 %). IR (KBr): 3444 (OH), 1638 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.57 (s, 2H, OH), 8.37 (s, 2H, CH=N), 7.02 (s, 2H, *m*-H), 7.00 (s, 4H, *m*-H), 3.46-3.38 (m, 2H, cyclohexyl-CH), 3.36-2.94 (m, 32H, NCH_2), 2.67 (quintet, *J* = 6.4 Hz, 2H, CH), 2.21 (s, 6H, CH_3), 1.92-1.82 (m, 4H, cyclohexyl-CH_2), 1.74-1.20 (m, 68H), 0.90 (t, *J* = 7.6 Hz, 18H, CH_3), 0.84 (t, *J* = 7.6 Hz, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.14, 158.02, 131.91, 131.61, 127.88, 126.00, 117.89, 72.26 (cyclohexyl-CH), 58.02 (NCH_2), 57.94 (NCH2), 40.66 (-CH-), 33.28 (-CH_2-), 33.11 (-CH_2-), 32.73 (-CH_2-), 23.98 (cyclohexyl-CH_2), 23.49 (butyl-CH_2), 19.88 and 19.79 (butyl-CH_2), 18.73 (cyclohexyl-CH_2), 15.61 (CH_3), 13.89 and 13.76 (butyl-CH_3) ppm. Anal. Calc. ($C_{84}H_{158}B_4F_{16}N_6O_2$): C, 61.84; H, 9.76; N, 5.15 %. Found: C, 61.54; H, 9.52; N, 5.49 %.

Synthesis of 6: This compound was synthesized using the same conditions and procedure as those for **8**, starting with **39**. A brown powder was obtained in quantitative yield. ^1H NMR (dmso-d_6, 38°C): δ 8.74 (br, 5H, $(NO_2)_2C_6H_3O$), 8.12 (br, 5H, $(NO_2)_2C_6H_3O$), 7.65 (s, 2H, CH=N), 7.33 (s, 2H, *m*-H), 7.20 (s, 2H, *m*-H), 6.81 (br, 5H, $(NO_2)_2C_6H_3O$), 3.58 (br, 2H, cyclohexyl-CH), 3.30-2.90 (m, 36H, cyclohexyl-CH_2 and NCH_2), 2.57 (br, 2H, CH), 2.00 (br, 2H, cyclohexyl-CH_2), 1.86 (br, 2H, cyclohexyl-CH_2), 1.70 (s, 18H, CH_3), 1.70-1.35 (br, 40H, CH_2), 1.30-1.10 (br, 24H, CH_2), 0.85 (br t, *J* = 7.2 Hz, 36H, CH_3) ppm. $^{13}C\{^1H\}$ NMR(dmso-d_6, 38 °C): δ 162.83, 161.73, 142.17, 131.15 (br), 130.86, 129.71 (X-C), 128.55, 128.16 (br, X-C), 123.41 (br, 2C, X-C), 118.66, 68.66 (cyclohexyl-CH), 57.13 (CH_2NCH_2), 41.91 (benzyl-CH), 35.13 (*t*Bu-C), 32.47 (2C, CH_2), 29.91, 29.04 (cyclohexyl-CH_2), 23.84 (cyclohexyl-CH_2), 22.58 (butyl-CH_2), 18.79 (*t*Bu-CH_3), 18.74 (butyl-CH_2), 12.97 (butyl-CH_3) ppm. Two 2,4-dinitrophenolate signals at ~165 and ~137 ppm were missing due to broadening. Anal. Calc. ($C_{120}H_{183}CoN_{16}O_{27}\cdot NaBF_4$): C, 58.81; H, 7.53; N, 9.15 %. Found: C, 58.46; H, 7.48; N, 9.10 %. HRMS (FAB): m/z calcd ($[M-2\{(NO_2)_2C_6H_3O\}+BF_4]^+$ $C_{102}H_{174}O_{12}N_{10}F_4BCo$) 1877.2674, found 1877.2666.

Synthesis of 7: This compound was synthesized using the same conditions and procedure as those for **8**, starting with **40**. A brown powder was obtained in quantitative yield. ^1H NMR (dmso-d_6, 38°C): δ 8.65 (br, 5H, $(NO_2)_2C_6H_3O$), 8.03 (br, 5H, $(NO_2)_2C_6H_3O$), 7.82 (s, 2H, CH=N), 7.29 (s, 2H, *m*-H), 7.15 (s, 2H, *m*-H), 6.75 (br, 5H, $(NO_2)_2C_6H_3O$), 4.05 (br, iPr-CH, 2H), 3.59 (br, 2H, cyclohexyl-CH), 3.30-2.90 (m, 36H, cyclohexyl-CH_2 and NCH_2), 2.54 (br, 2H, CH), 2.05 (br, 2H, cyclohexyl-CH_2), 1.83 (br, 2H, cyclohexyl-CH_2), 1.70-1.35 (br, 52H, CH_2), 1.30-1.10 (br, 24H, iPr-CH_3 and CH_2), 0.85 (br, 36H, CH_3) ppm. $^{13}C\{^1H\}$ NMR(dmso-d_6, 38 °C): δ 165.61 (br, X-C), 163.75 (br), 161.78, 142.18, 137.06 (br, X-C), 132.61, 131.36, 130.30 (br, X-C), 128.94 (2C, Salen-C and X-C), 124.30 (2C, X-C), 118.85, 70.09 (cyclohexyl-CH), 58.58 (CH_2N), 58.39 (NCH_2), 43.25 (benzyl-CH), 33.67 (2C, CH_2), 30.28 (iPr-CH), 29.21 (cyclohexyl-CH_2), 25.20 (iPr-CH_3), 24.36 (cyclohexyl-CH_2), 23.86 (butyl-CH_2), 23.49 (iPr-CH_3), 20.02 (butyl-CH_2), 14.24 (butyl-CH_2) ppm. Anal. Calc. ($C_{118}H_{179}CoN_{16}O_{27}\cdot NaBF_4$): C, 58.50; H, 7.45; N, 9.25 %. Found: C, 57.96; H, 7.28; N, 9.37 %. HRMS (FAB): m/z calcd ($[M-2\{(NO_2)_2C_6H_3O\}+BF_4]^+$ $C_{100}H_{170}O_{12}N_{10}F_4BCo$) 1849.2361, found 1849.2351.

Synthesis of 8: Cobalt(II) acetate (0.014 g, 0.079 mmol) and ligand **41** (0.128 g, 0.079 mmol) were dissolved in ethanol (6 mL) inside a glove box. The resulting red solution was stirred for 3.5 hours at room temperature. The solvent was removed under vacuum to give a red solid that was subsequently triturated two times in diethyl ether (5 mL) to remove acetic acid that had been generated. The solid was dissolved in CH_2Cl_2 (6 mL) containing 2,4-dinitrophenol (0.015 g, 0.079 mmol), and the solution was stirred under an O_2 atmosphere for 3 hours. Sodium-2,4-dinitrophenolate (0.081 g, 0.39 mmol) was added. After the solution was stirred overnight at room temperature, it was filtered over Celite. The solvent was removed under vacuum to give a dark brown powder that was pure enough to be used for polymerization. Yields were quantitative (0.175 g). The CHN elemental analysis data deviated a little from the calculated values, but they were well in agreement with the structure containing additional 1.0 equivalent $NaBF_4$. We presume that some $NaBF_4$ was extracted out into CH_2Cl_2 phase during the final salt exchange reaction. We also observed a characteristic BF_4 signal in the ^{19}F NMR. In the high resolution mass (FAB) study, the corresponding M-2[2,4-$(NO_2)_2C_6H_3O$] signal, which was observed for **3-5**, was weak, but a fairly strong signal corresponding to M-3[2,4-$(NO_2)_2C_6H_3O$]+BF_4 was observed. ^1H NMR (dmso-d_6, 70 °C): δ

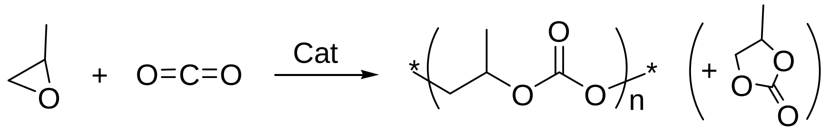
8.62 (br, 5H, $(NO_2)_2C_6H_3O$), 8.06 (d, *J* = 8.0 Hz, 5H, $(NO_2)_2C_6H_3O$), 7.67 (s, 2H, CH=N), 7.27 (s, 2H, *m*-H), 7.15 (s, 2H, *m*-H), 6.91 (br, 5H, $(NO_2)_2C_6H_3O$), 3.83 (br s, 2H, cyclohexyl-CH), 3.30-2.96 (m, 36H, cyclohexyl-CH_2 and NCH_2), 2.67 (s, 6H, CH_3), 2.54 (br s, 2H, CH), 2.10-2.00 (br , 2H, cyclohexyl-CH_2), 1.96-1.80 (br, 2H, cyclohexyl-CH_2), 1.68-1.42 (m, 40H, CH_2), 1.24 (m, 24H, CH_2), 0.86 (t, *J* = 7.2 Hz, 36H, CH_3) ppm. $^{13}C\{^1H\}$ NMR(dmso-d_6, 38 °C): δ 164.56 (br, X-C), 162.66 (br), 161.37, 136.34 (br, X-C), 133.09, 131.47, 130.40, 128.82 (br, 2C, Salen-C and X-C), 127.91 (X-C), 123.24 (2C, X-C), 117.05, 69.20 (cyclohexyl-CHN), 57.32 (CH_2NCH_2), 41.70 (benzyl-CH), 32.70 (CH_2), 32.49 (CH_2), 29.22 (cyclohexyl-CH_2), 24.12 (cyclohexyl-CH_2), 22.76 (butyl-CH_2), 18.89 (butyl-CH_2), 16.92 (benzyl-CH_3), 13.09 (butyl-CH_3) ppm. Anal. Calc. ($C_{114}H_{171}CoN_{16}O_{27}\cdot NaBF_4$): C, 57.86; H, 7.28; N, 9.47 %. Found: C, 57.67; H, 7.29; N, 9.42 %. HRMS (FAB): m/z calcd ($[M-2\{(NO_2)_2C_6H_3O\}+BF_4]^+$ $C_{96}H_{162}O_{12}N_{10}F_4BCo$) 1793.1735, found 1793.1741.

Synthesis of silver 2,4-dinitrophenolate: To a solution of KOH (0.913 g, 16.3 mmol) in H_2O (70 mL), 2,4-dinitrophenol (3.60 g, 16.3 mmol) was added as a solid. The solution was heated to yield a clear solution. The resulting solution was filtered, and a solution of $AgNO_3$ (2.80 g, 16.3 mmol) in H_2O (10 mL) was added. A solid precipitated immediately, was collected by filtration, and was washed with H_2O (2 × 20 mL). The resulting orange solid was dried under vacuum overnight at 40°C. The yield was 3.80 g (80%).

Synthesis of tetrabutylammonium 2,4-dinitrophenolate: Tetrabutylammonium bromide (0.554 g, 1.72 mmol) and silver 2,4-dinitrophenolate (0.500 g, 1.72 mmol) were weighed into a one-neck flask, and ethanol (20 mL) was added. The solution was stirred at room temperature overnight in the dark. The generated AgBr was filtered off, and the solvent was removed under vacuum to give a yellow solid. The solid was redissolved in CH_2Cl_2 (10 mL), and then the solution was filtered again. Removal of the solvent afforded the product as a yellow solid in quantitative yield. ^1H NMR ($CDCl_3$): δ 8.83 (d, *J* = 2.8 Hz, 1H), 7.87 (dd, *J* = 9.6, 3.2 Hz, 1H), 6.58 (d, *J* = 10.0 Hz, 1H), 3.23-3.18 (m, 8H, NCH_2), 1.60 (quintet, *J* = 8.4 Hz, 8H, CH_2), 1.38 (sextet, *J* = 7.2 Hz, 8H, CH_2), 0.95 (t, *J* = 6.8 Hz, 12H, CH_3) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 170.63, 135.82, 129.51, 127.87, 126.40, 125.52, 58.65, 23.83, 19.67, 13.62 ppm.

CO_2/(propylene oxide) copolymerization (small scale). Into a bomb reactor (50 mL), inside a glove box, the complex [3.5 mg for [PO]/[Cat] = 100000 and **8** (entry 8 in Table 1)] and propylene oxide (10.0 g, 172 mmol) were added. The bomb reactor was assembled and immersed in an 80°C oil bath. It was stirred for 15 minutes to allow the solution temperature to reach the bath temperature. The CO_2 gas was pressurized to 20 bar. As the polymerization proceeded, a pressure drop was observed. After running for the time indicated in Table S1 below, the reactor was cooled to room temperature by immersing it in an ice bath. After the CO_2 gas was released, the reactor was opened. An aliquot was taken and dissolved in $CDCl_3$. ^1H NMR analysis of the solution allowed for calculation of the selectivity and the carbonate linkage. The viscous solution was transferred to a one-neck flask and the unreacted PO was removed using a rotary evaporator. Additional information regarding the polymerization results is provided in Table S1 below. In Table 1, the activity (TOF) increases either by reducing the bulkiness of *ortho*-substituent or by increasing the number of quaternary ammonium salt units. Steric bulkiness on the *ortho*-position might hinder the attack of the carbonate anion on the coordinated epoxide, consequently decreasing the reaction rate. As the atomic radius decreases by the increase of the atomic number in the same period of the periodic table of the elements, the average distance between the metal center and the carbonate anion may become shorter by increasing the number of quaternary ammonium units. Through positioning the chain-growing carbonate anion closer to the cobalt center, we can expect a faster reaction rate. The selectivity is described by the term of R_p/R_{bb} (R_p = rate of polymerization; R_{bb} = rate of back-biting). The R_{bb} is not influenced by the nature of the metal center because the back-biting occurs at a free chain end. So, the selectivity increases by the increase of TOF, which is in agreement with the data in Table 1.

Table S1. Additional Information for CO_2/(propylene oxide) copolymerization results.[a]



Entry	Cat	[PO]/[Cat]	t (h)	Yield (g)	TOF[b] (h^{-1})	TON	Selectivity[c]	M_n[d] $\times 10^{-3}$	M_w/M_n	Conversion (%)[e]	Head-to-Tail linkage (%)	Carbonate linkage (%)
1	**3**	25000	6.0	1.15	270	1600	70	42	1.20	6.4	76	100
2	**4**	25000	1.0	2.20	3100	3100	95	11	1.49	12	74	100
3	**5**	25000	1.0	2.10	3000	3000	89	36	1.52	12	82	100
4	**6**	25000	2.0	1.85	1300	2600	84	38	1.34	10	85	100
5	**7**	25000	0.67	3.80	7900	5300	>99	76	1.32	21	89	100
6	**8**	25000	0.25	4.55	26000	6400	>99	114	1.29	26	89	100
7	**8**	50000	0.50	4.60	26000	13000	>99	208	1.20	26	89	100
8[f]	**8**	100000	1.5	3.90	22000	22000	>99	280	1.18	22	89	100
9[f]	**8**	100000	2.0	4.80	18000	27000	92	225	1.28	27	86	100
10[f]	**8**	150000	5.5	3.70	12400	31000	96	175	1.20	21	82	100
11	**2**	25000	1.0		3300	3300	94	71	1.25	13		100
12	**1**	2000	0.70		1400	980	97	26	1.01	49		100

[a] Polymerization condition: Propylene oxide (10.0 g, 172 mmol), CO_2 (2.0 - 1.7 MPa), bath temperature of 80°C. [b] Calculated based on the weight of the isolated polymer not including the cyclic carbonate. [c] Selectivity for the polycarbonate over the cyclic carbonate in unit of % determined by the ^{1}H NMR spectroscopy of the crude product. [d] Determined on GPC using the polystyrene standard [e] 100×(Mole of the reacted PO)/(mole of the charged PO). [f] We observed some induction time (~30 min for entries 8 and 9, ~3 hours for entry 10) which was excluded in calculating TOF.

CO_2/(propylene oxide) copolymerization (90 g scale). A bomb reactor (500 mL scale) equipped with a mechanical stirrer was evacuated at 145°C for 3 hours. After the reactor was cooled to room temperature, PO (~240 g) was charged using a cannula. A solution of **8** (0.095 g, 0.043 mmol) in PO (~10 g, making total PO = 250 g) was added using a syringe. After the solution was heated to 65°C, CO_2 gas was charged to 20 bar. The charge rapidly increased the solution temperature to 71°C, possibly due to the heat of dissolution of CO_2 to PO. The solution temperature remained at ~71°C for ~15 minutes, after which it gradually increased to 77°C due to the heat of polymerization. After that, the reaction temperature remained at 77-75°C. The initial stirring rate was ~420 rpm, but when the stirring power was not changed during polymerization, it decreased gradually. We terminated the polymerization when the stirring rate had dropped to ~270 rpm; running the polymerization beyond that point slighly increased TON, but it detrimentally sacrificed the selectivity and TOF. When the stirring rate reached ~270 rpm, the reactor was immersed in an ice bath to cool it to below 35 °C. After the CO_2 pressure was released, the reactor was opened. An aliquot was taken for NMR analysis. The thick viscous solution was diluted with PO (250 g). The light yellow solution was filtered through a short pad of silica gel (12 g), which had been wetted with PO (40 mL) *containing the copolymer* (5.0 g). When the silica gel pad was not wetted, filtration was impossible; when it was wetted with PO without the copolymer, we occasionally observed formation of cracks in the silica gel pad, through which some of the catalyst passed, consequently lowering the catalyst separation yield. From the colourless filtrate, PO was removed by vacuum-transferring to a reservoir containing CaH_2. After drying over CaH_2 for several days, the recovered PO was used for the polymerization. The polymer adhered strongly to glass surfaces making it difficult to detach, but it was easily detachable by wetting it with diethyl ether, in which the copolymer is insoluble. The polymer lump was taken out of the flask and then broken manually to pieces. After the polymer pieces were placed in a hood overnight to evaporate some residual PO, they were completely dried in an oven (~150°C) for 30 minutes. The residual PO could not be completely removed by evacuation at room temperature alone. Additional information for the 90 g-scale polymerization using the recovered catalyst of **8** is provided in Table S2. A picture of the light-yellow viscous polymerization solution (entry 1 in Table 2) and a picture of the filtration are provided below. For comparison, a picture showing filtration of the polymerization solution prepared with a binary catalytic system consisting of [(Salen)Co complex]/(PPN^+Cl^-) (**1**), in which the quaternary ammonium salt was not bound with Salen-unit, is provided below. In this case, the (Salen)Co complex was not collected on the silica gel pad but passed through it, making the filtrate deep red. Pictures of the polymer isolated after filtration through silica gel pad and the polymer isolated without the filtration procedure are provided below as well. The GPC curve of the polymer is provided where we observe a narrow bimodal shape. The TGA and DSC curves of a high molecular-weight sample (M_n = 296000, the 1st run in Table 2) are also provided below. The copolymer decomposed at ~230 °C and nothing remained above 290 °C. The glass transtion temperature (T_g) was 38 °C.

Table S2. Additional Information for 90-g scale CO_2/(propylene oxide) copolymerization using the recovered catalyst of **8**.[a]

run #	t (h)	Yield (g)	TOF[b] (h^{-1})	TON	Selectivity[c]	M_n[c] $\times 10^{-3}$	M_w/M_n	Head-to-Tail linkage (%)	Carbonate linkage (%)
1st	65	92	19000	21000	>99	296	1.19	86	100
2nd	85	90	15000	21000	98	172	1.41	87	100
3rd	85	89	15000	21000	97	176	1.34	86	100
4th	80	88	16000	21000	98	190	1.22	85	100
5th	90	85	13000	20000	97	210	1.21	85	100

[a] Polymerization condition: Propylene oxide (250 g), catalyst **8** (95 mg), [PO]/[Cat] ratio = 100000, 70-77°C of polymerization solution temperature, CO_2 pressure of 2.0 Mpa.

Catalyst recovery: After filtration of the polymer solution prepared in 90 g-scale, the orange-coloured upper part of the silica gel pad was collected and treated with a concentrated $NaBF_4$ solution in methanol (~ 30 mL). The resulting slurry was filtered and washed with a concentrated methanol solution of $NaBF_4$ until the filtrate became colourless. The solvent was removed under vacuum. CH_2Cl_2 (20 mL) was added to the residue, and the solution was filtered to remove the insoluble $NaBF_4$. The solvent was removed to give a dark brown solid. The solid was dissolved in CH_2Cl_2 (3 mL). A mixture of sodium 2,4-dinitrophenolate and 2,4-dinitrophenol in a 3:2 mole ratio (0.043 g, 2.0 equivalents of 2,4-dinitrophenol and 4.0 equivalents of sodium 2,4-dinitrophenolate based on the added complex in the polymerization), which had been prepared by adding 0.60 equivalent of NaH in 2,4-dinitrophenol solution in THF, was added, and the solution was stirred overnight at room temperature. After the solution was filtered over Celite, the solvent was removed under vacuum to give a dark brown solid that was subsequently triturated in anhydrous diethyl ether. The ^{1}H NMR spectra of the recovered catalyst after five successive runs and that of virgin catalyst are provided below for comparison. In the polymerizations with the recovered catalyst (entries 2-5 in Table 2), polymerization started after 30-40 minutes later from the CO_2 injection, after which the rate of polymerization was almost same with that observed for fresh, virgin catalyst **8**. We presume that the induction time observed for entries 8-10 in Table 1 and here may be attributed to the time needed to scrub water present as an impurity in the polymerization pot. It was reported that water blocked this copolymerization.[7] It was also well reported that Salen-cobalt complex acted as a catalyst transforming water to propylene diol in the presence of propylene oxide.[8] We presume that, at the initial induction period, the cobalt complex worked to convert water to propylene diol. After all the water present as an impurity was converted to proylene diol, the polymerization might start. We proved that the alcohol such as propylene diol did not block the polymerization but acted as a chain transfer reagent to lower the molecular weight. During the catalyst recovery, some water might be accompanied with the recovered catalyst, resulting in longer induction time and lower molecular weight.

The ^{1}H NMR spectrum of the extracted complex, which is attached below, was messy, not-assignable especially in the aromatic region. We indirectly proved that the extracted one was the dihydroxylato complex proposed in Scheme 2. The ^{1}H NMR spectrum of a complex prepared through the treatment of aqueous KOH solution to a CH_2Cl_2 solution of complex **8** ($X = BF_4^-$) is almost identical to that of the extracted one (See the spectrum attached below). The ^{1}H NMR spectrum of complex **8** ($X = BF_4^-$), which is attached below either, is clean and assignable. One might expect an exchange reaction of the hydroxyl ligand with methoxy ligand during the methanol extraction process, but we did not observe the methoxy signal in the ^{1}H NMR spectrum. The exchange reaction is not favorable for Salen cobalt(III) complex. If the exchange reaction is favorable, the polymerization reaction might not be quenched by the addition of water. The fact that the addition of small amount of water completely blocks the polymerization reaction implies that the reverse reaction - exchange of the alkoxy with a hydroxyl ligand - is thermodynamically highly favorable.

Preparation of sample for ICP-MS: A sample of the isolated polymer prepared in 90-g scale (300 mg each for entries 1 and 2 in Table 2) was taken in a one-neck flask and concentrated nitric acid (69%, 4.00 g) was added. The resulting mixture was heated at 45°C until the polymer was completely dissolved. Concentrated sulfuric acid (18.0 g) was added, and the solution was kept at room temperature for 24 hours. A part of the solution (553 mg and 564 mg for entries 1 and 2 in Table 2, respectively) was placed into a one-neck flask, and the nitric and sulfuric acids were distilled off under vacuum at 200°C. The residue was dissolved in 1.0% nitric acid (19.67 g and 19.64 g for entries 1 and 2 in Table 2, respectively), and the sample was analyzed by the ICP-MS for cobalt. Measured cobalt levels were 1.090 ppb and 0.796 ppb for entries 1 and 2, respectively. A blank sample was also prepared by following exactly the same procedure, except no polymer was added; 0.297 ppb cobalt was measured in the blank sample, and this background was subtracted from the cobalt levels measured for the samples from entries 1 and 2. Measured cobalt levels correspond to 2.1 and 1.3 ppm-Co contents in the isolated polymers for entries 1 and 2 in Table 2, respectively.

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Figure S1. Viscous polymerization solution prepared in 90-g scale (21% conversion, entry 1 Table 2)

Figure S2 (Left). The filtration of the polymerization solution prepared with **8** (entry 1 in Table 2)

Figure S3 (Right). Silica gel filtration of the polymerization solution prepared with a binary system of [(Salen)Co complex]/(PPN^+Cl^-) (**1**)

Figure S4 (Left). Polymer isolated by the filtration through a silica gel pad (entry 1 in Table 2)

Figure S5 (Right). Polymer isolated without the filtration procedure (entry 8 in Table 1, [PO]/[Cat] = 100000)

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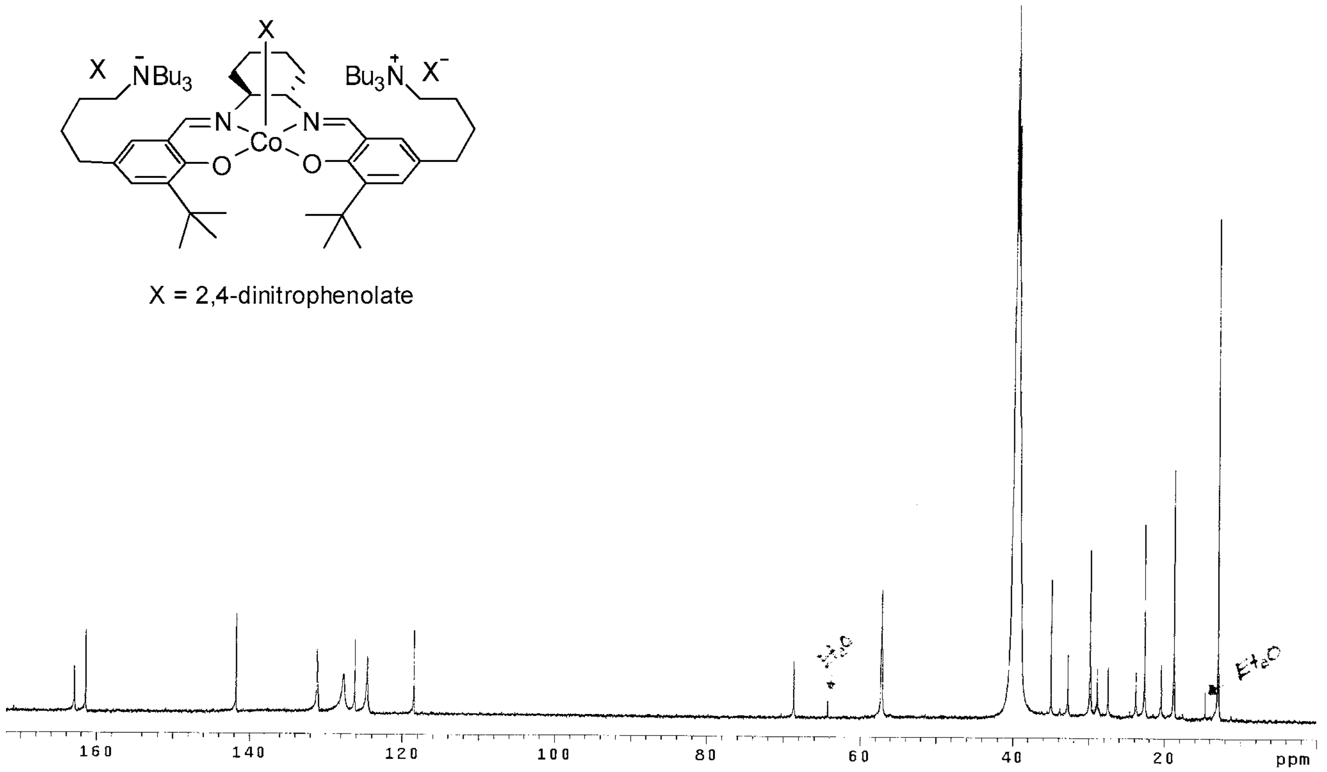
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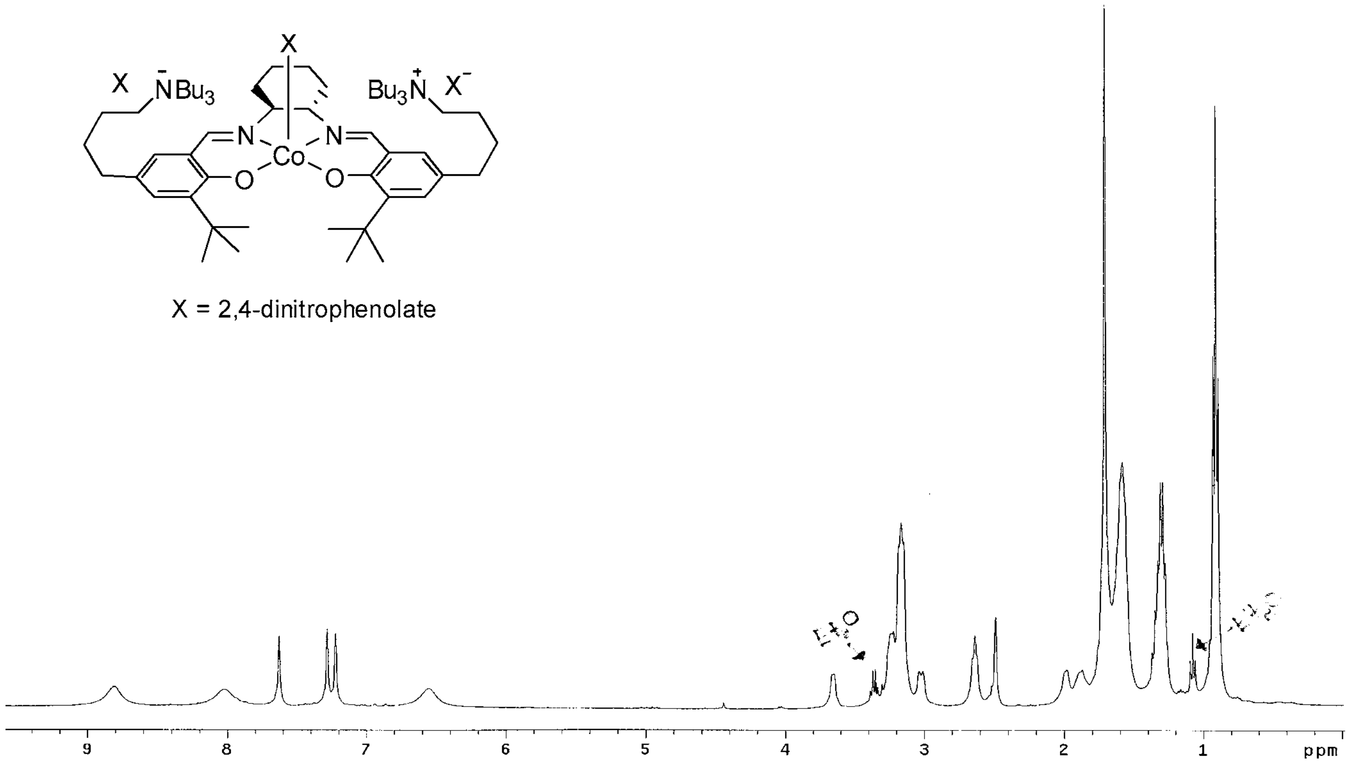
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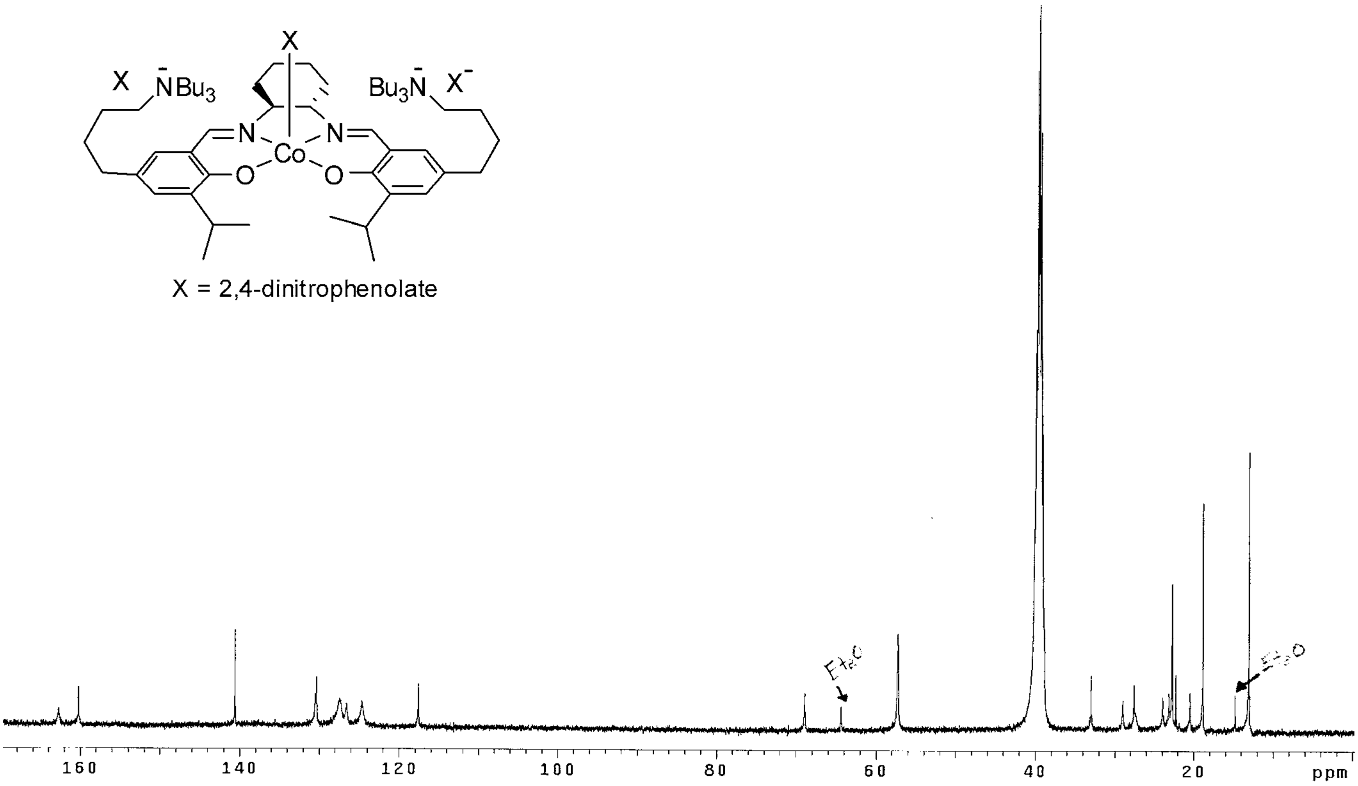
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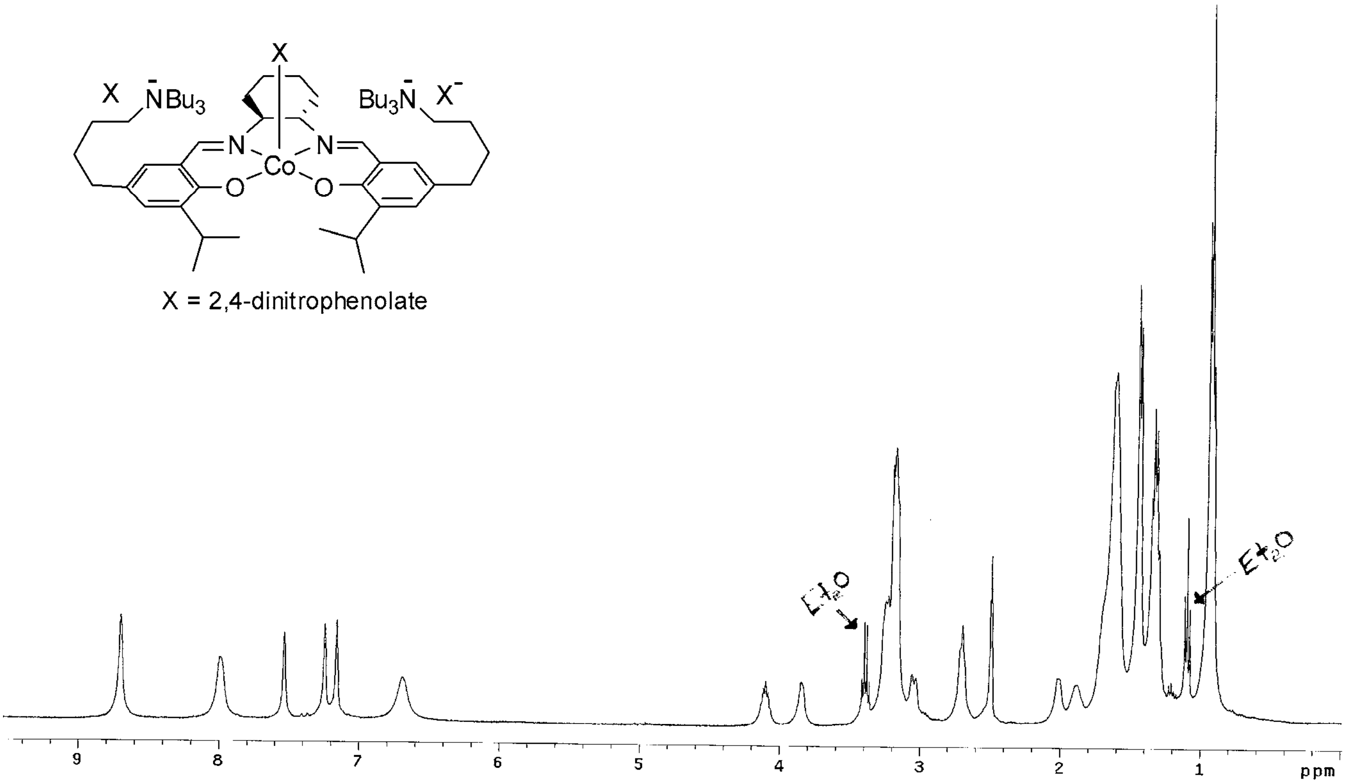
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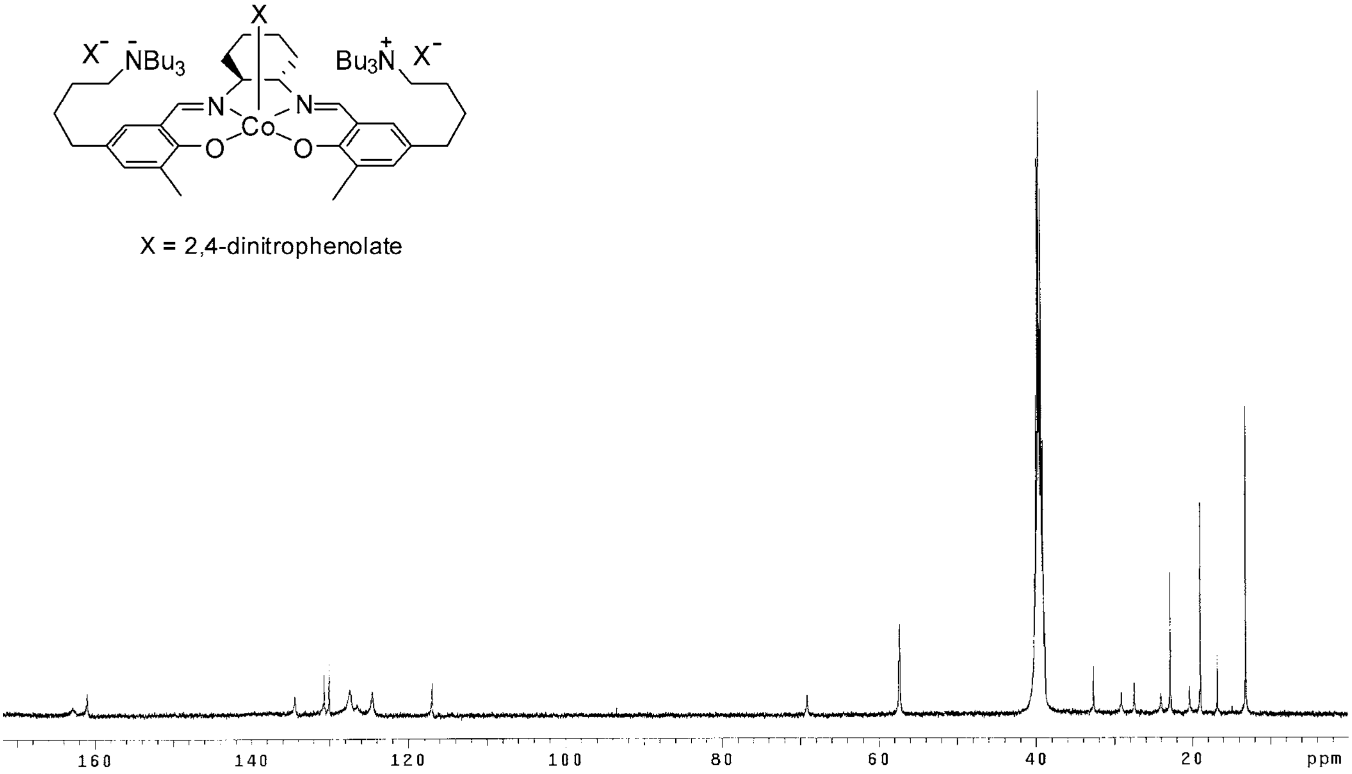
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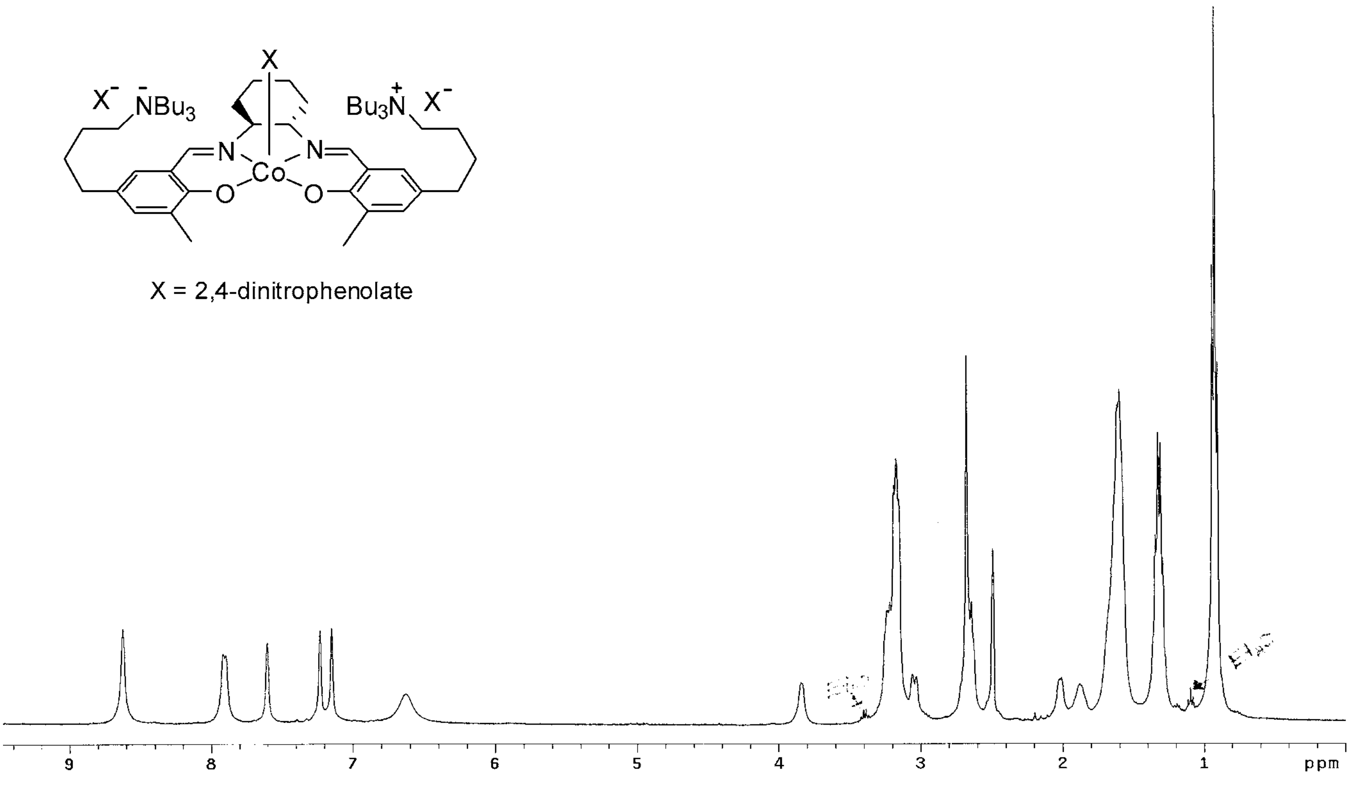
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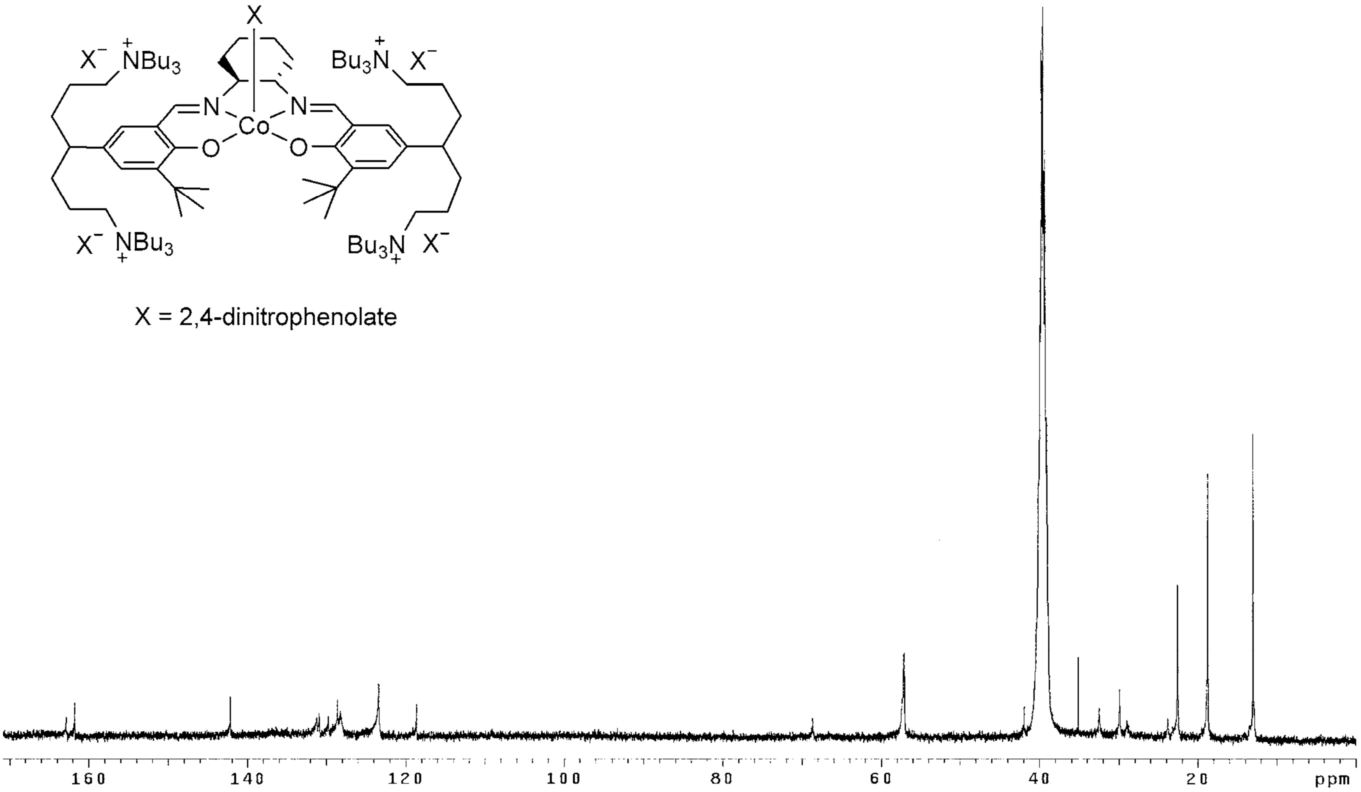
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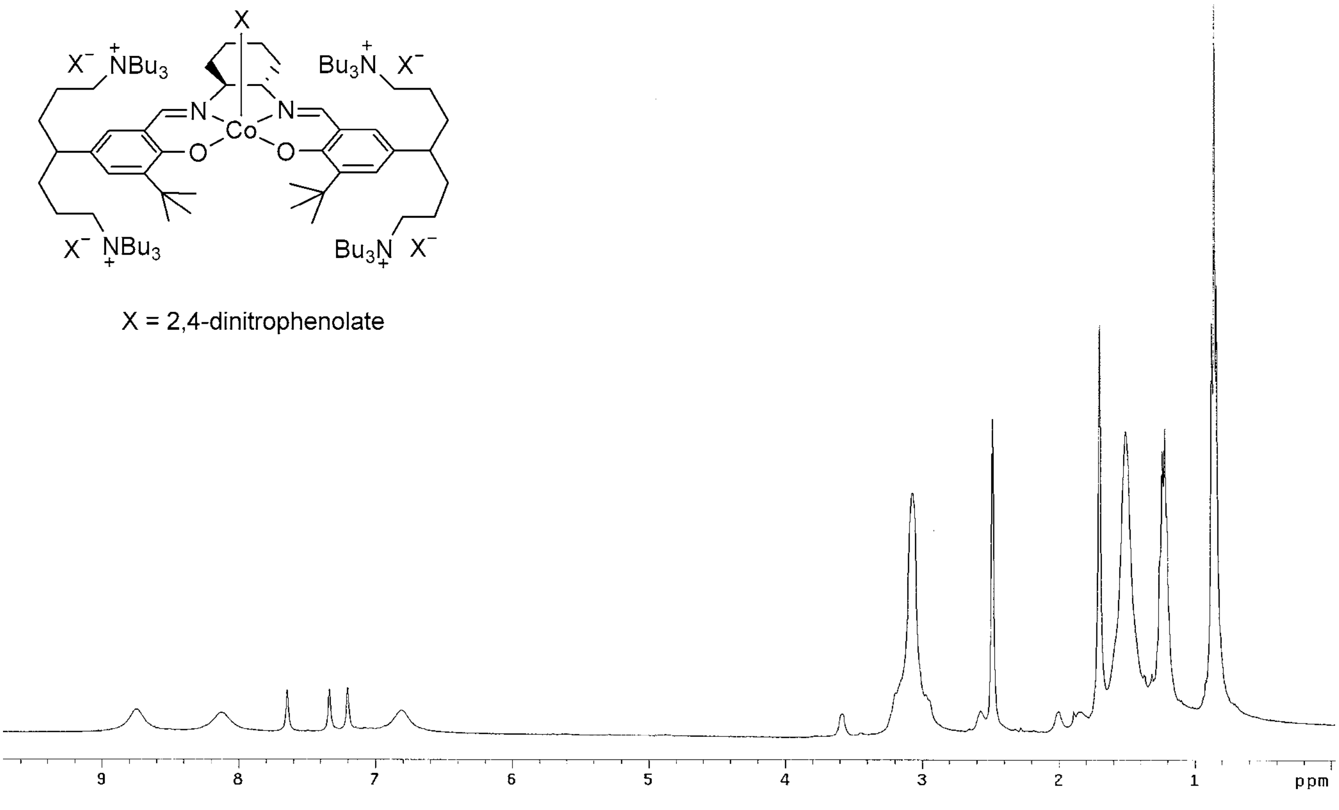
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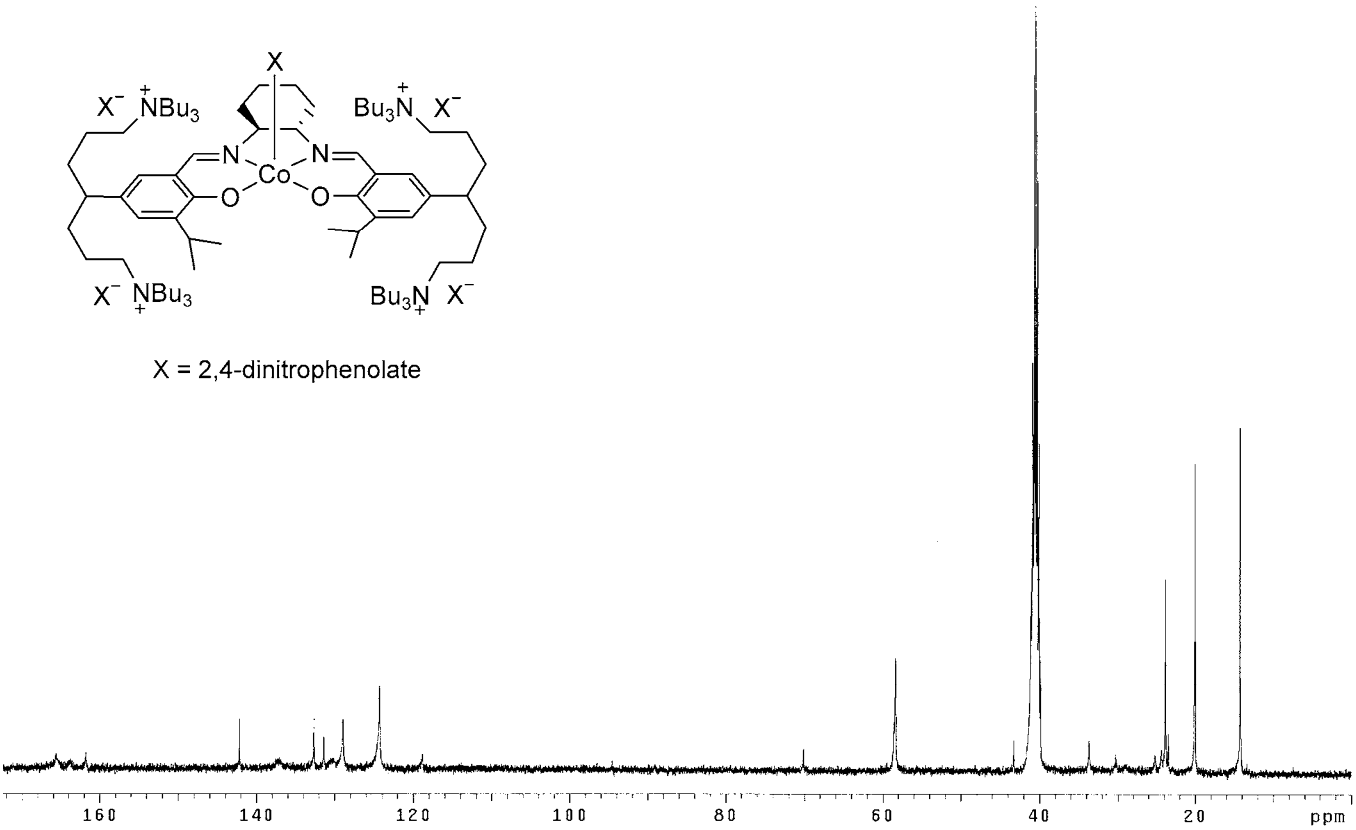
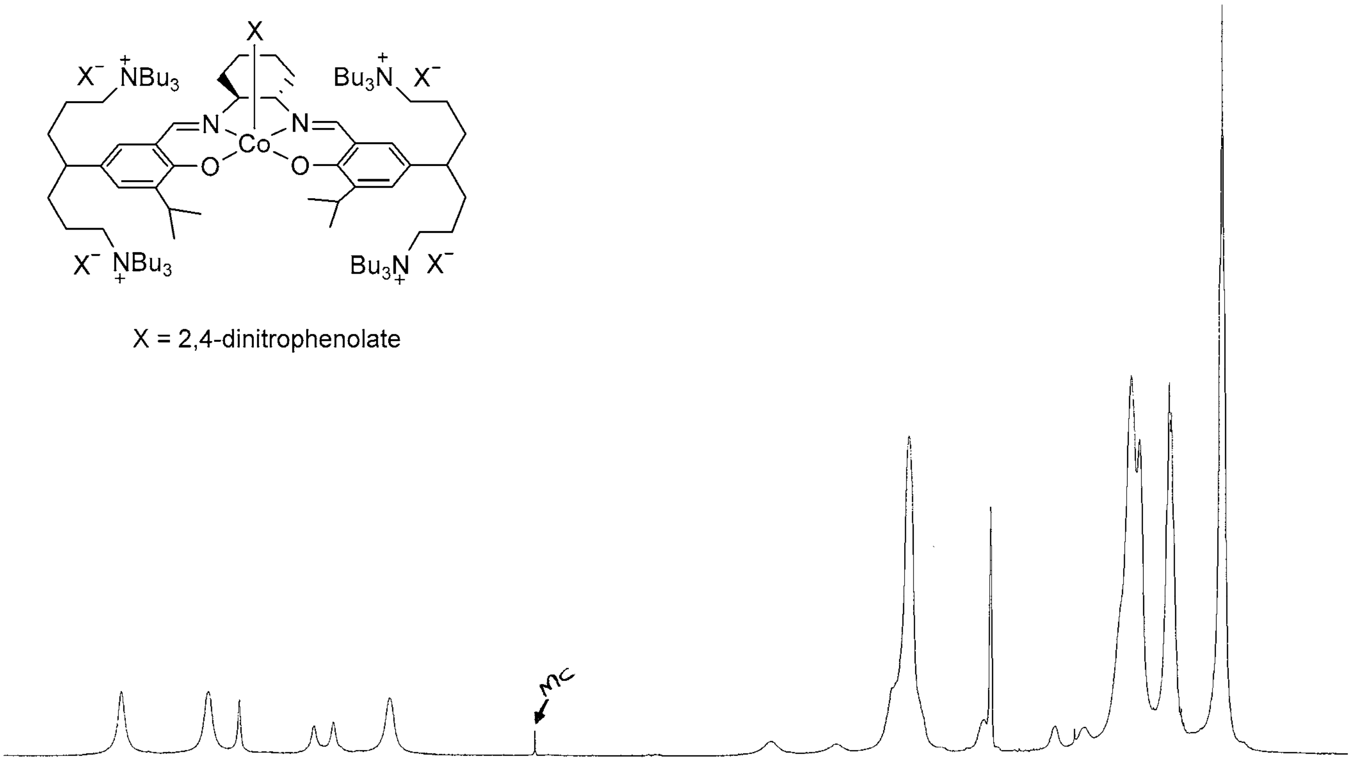
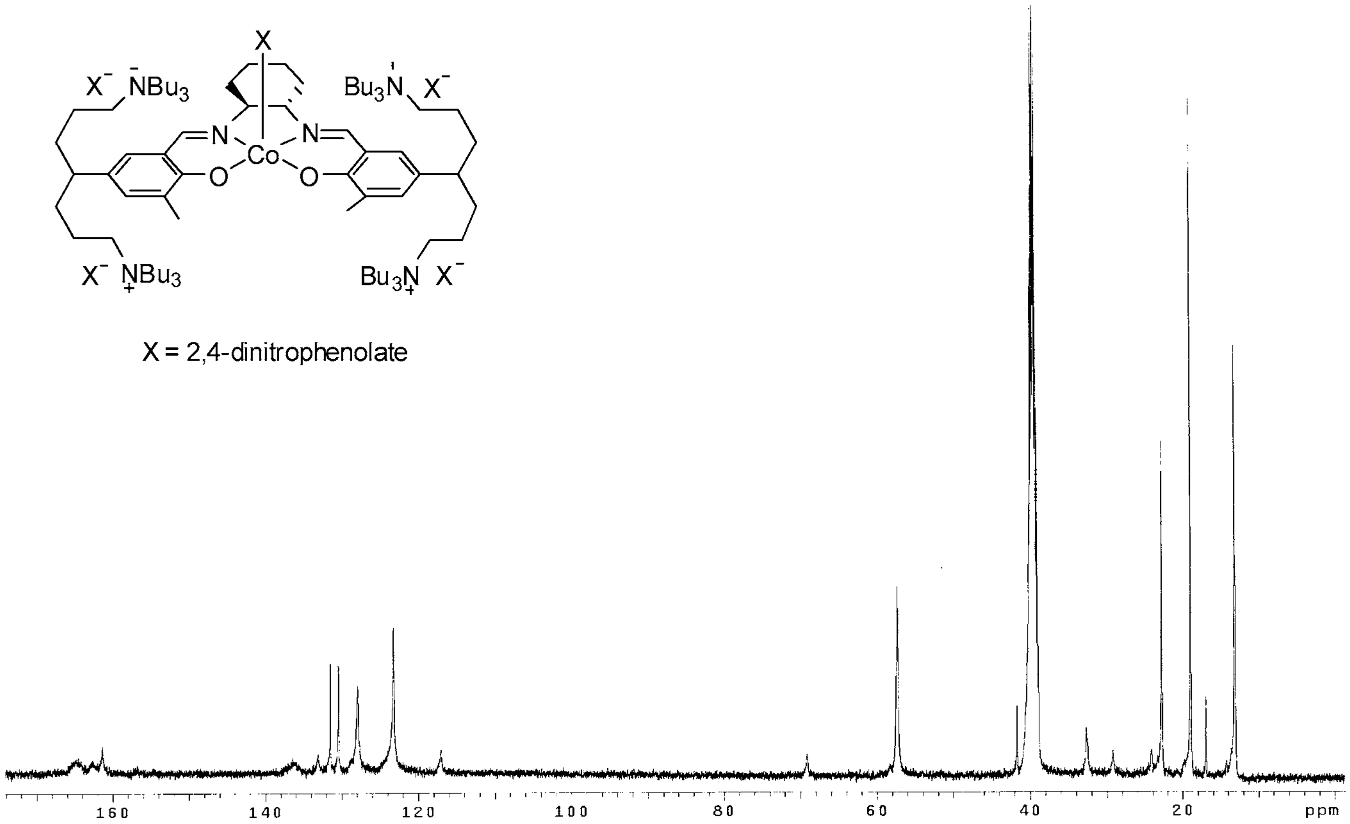
<The ^{13}C NMR spectrum (dmso-d$_6$, 38°C) of **7**>


X
X⁻ NBu3
Bu3N X⁻
N
Co
N
O
O
X⁻ NBu3
Bu3N X⁻
X = 2,4-dinitrophenolate
160
140
120
100
80
60
40
20
ppm

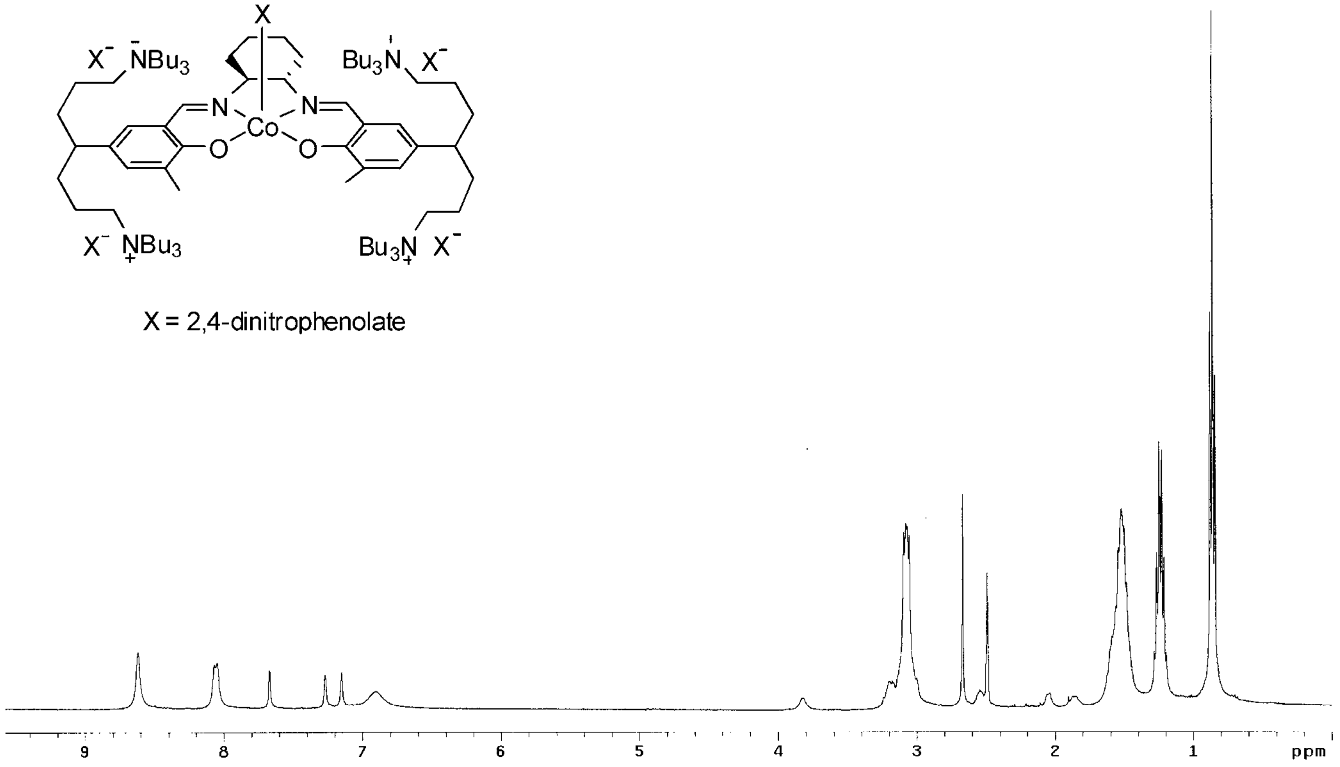
<The ^{1}H NMR spectrum (dmso-d$_6$, 70°C) of **7**>


X
X⁻ NBu3
Bu3N X⁻
N
Co
N
O
O
X⁻ NBu3
Bu3N X⁻
X = 2,4-dinitrophenolate
mc
9
8
7
6
5
4
3
2
1
ppm

<The ^{13}C NMR spectrum (dmso-d$_6$, 38^{o}C) of **8**>

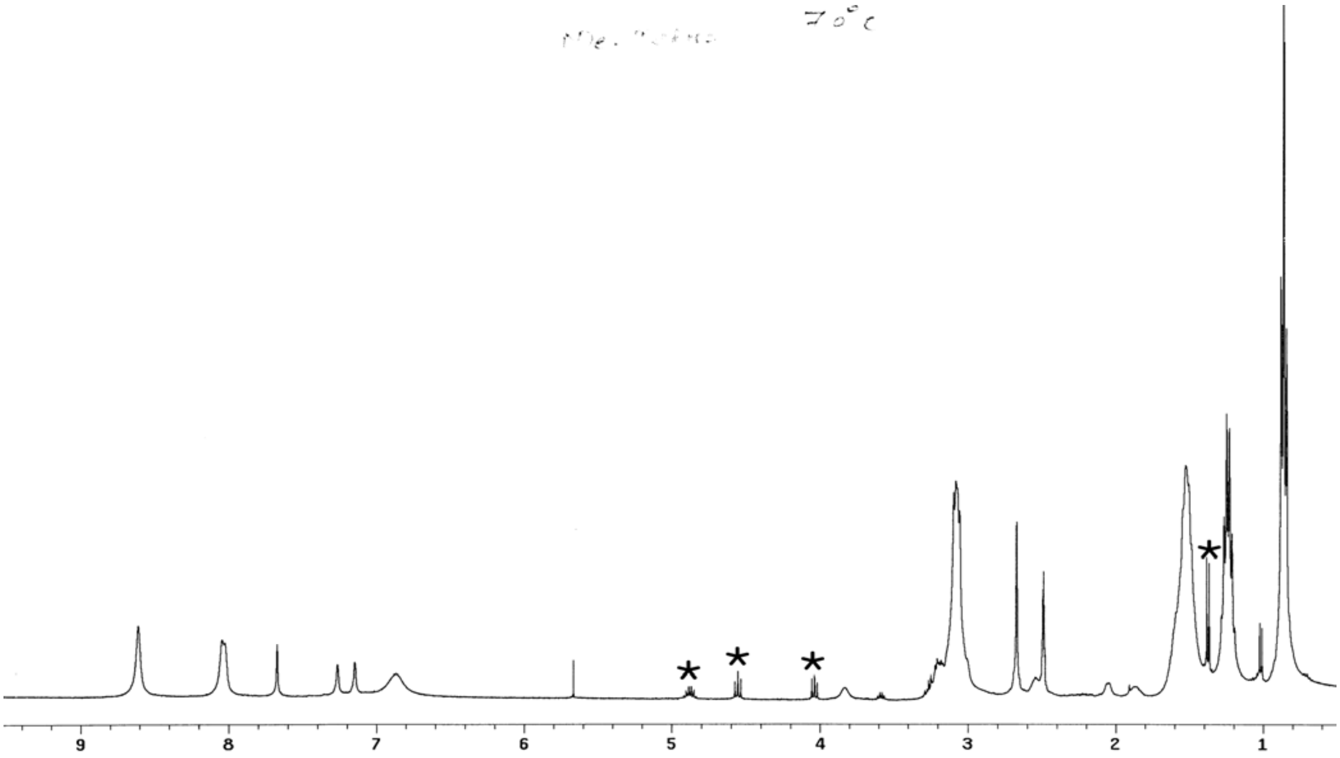

X
X⁻ NBu3
Bu3N X⁻
N
N
Co
O
O
X⁻ NBu3
Bu3N X⁻
X = 2,4-dinitrophenolate
160
140
120
100
80
60
40
20
ppm

<The ^{1}H spectrum (dmso-d$_6$, 70^{o}C) of **8**>

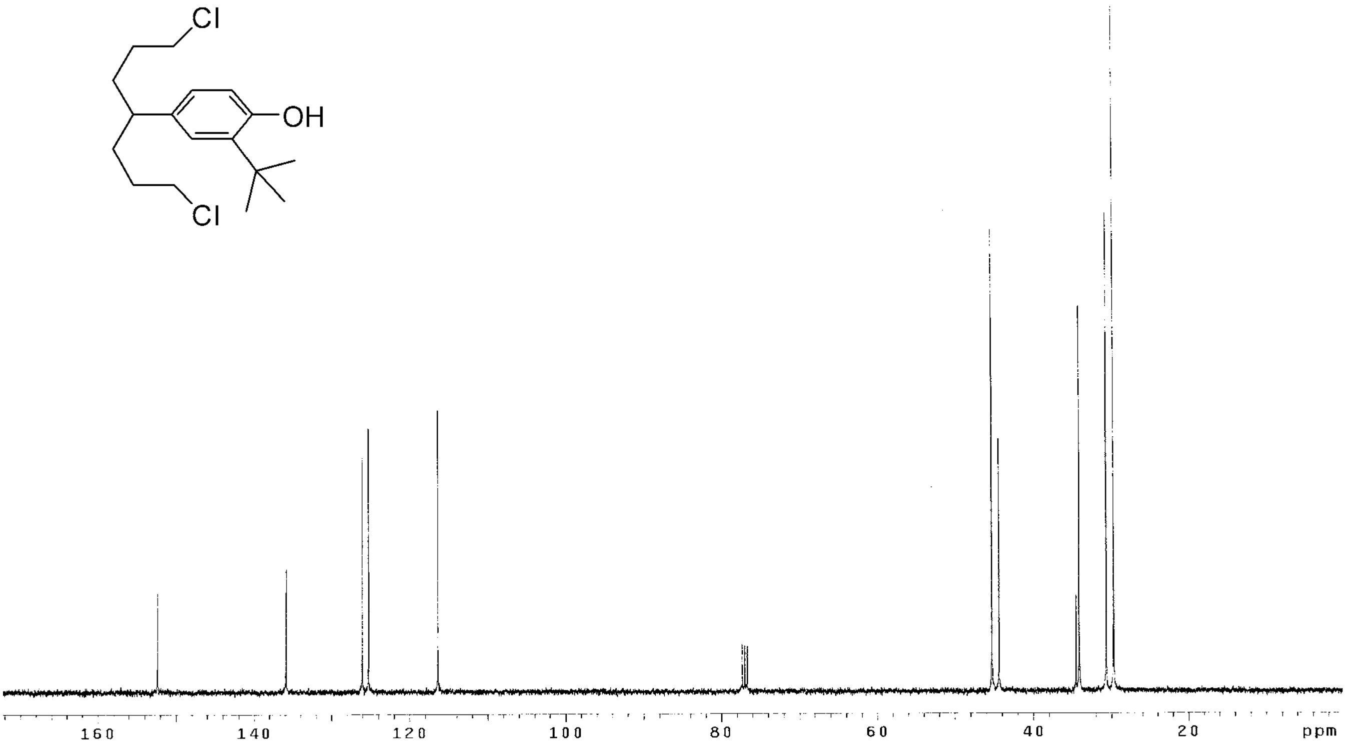

X
X⁻ NBu3
Bu3N X⁻
N
N
Co
O
O
X⁻ NBu3
Bu3N X⁻
X = 2,4-dinitrophenolate
9
8
7
6
5
4
3
2
1
ppm

<The ^{1}H NMR spectrum (dmso-d_6, 70°C) of the recovered catalyst **8** after five successive runs>

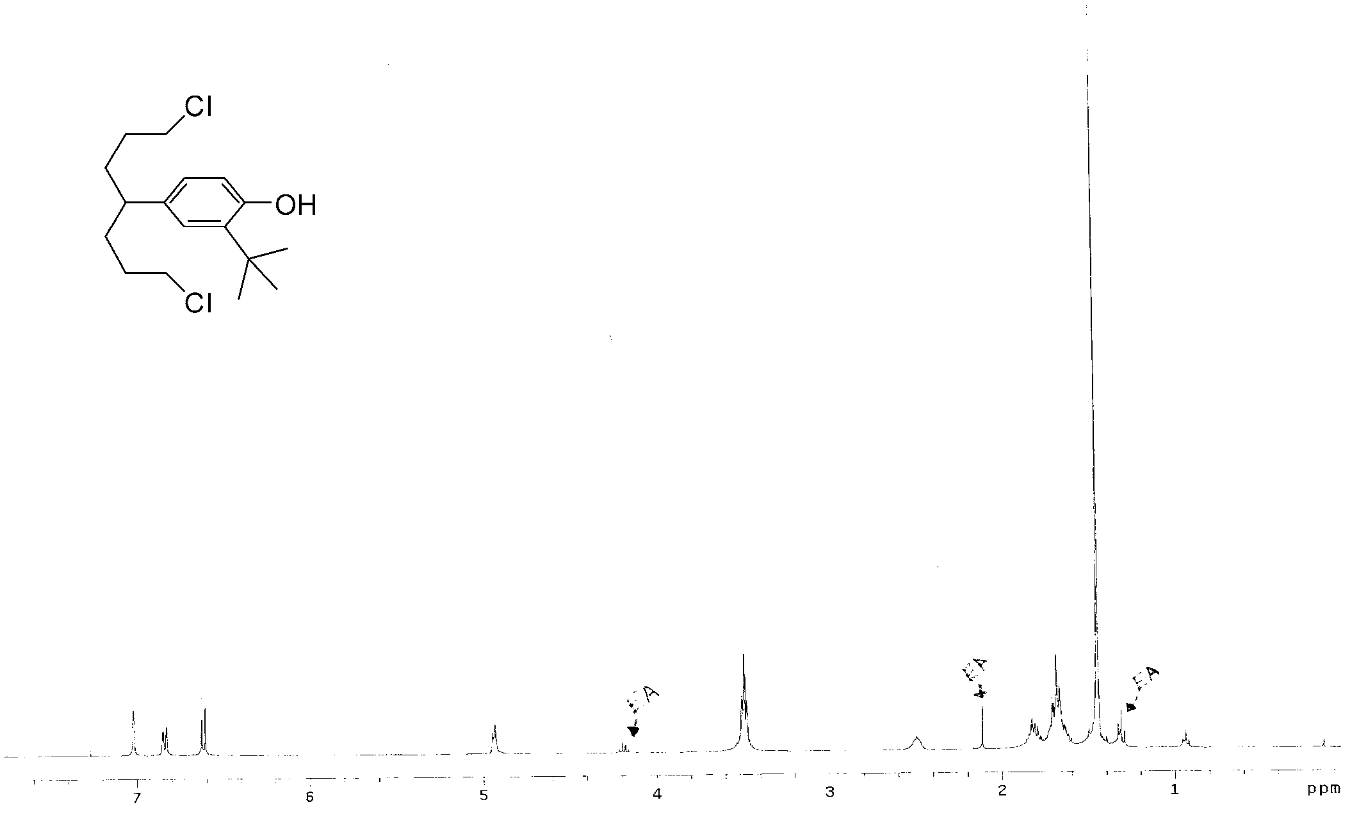
Signals marked with asterisks are the cyclic carbonate signals.



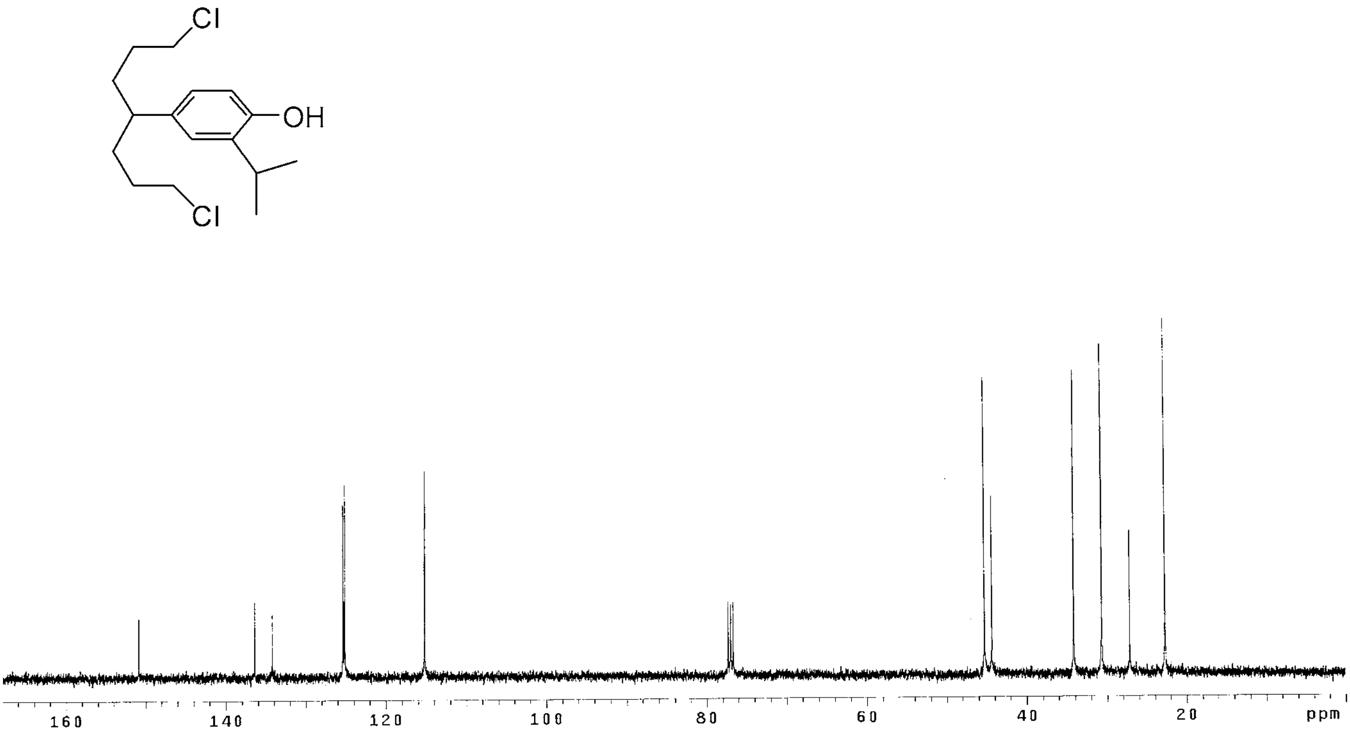
<The ^{13}C NMR spectrum (CDCl$_3$, 25°C) of **27**>


Cl
OH
Cl
160
140
120
100
80
60
40
20
ppm

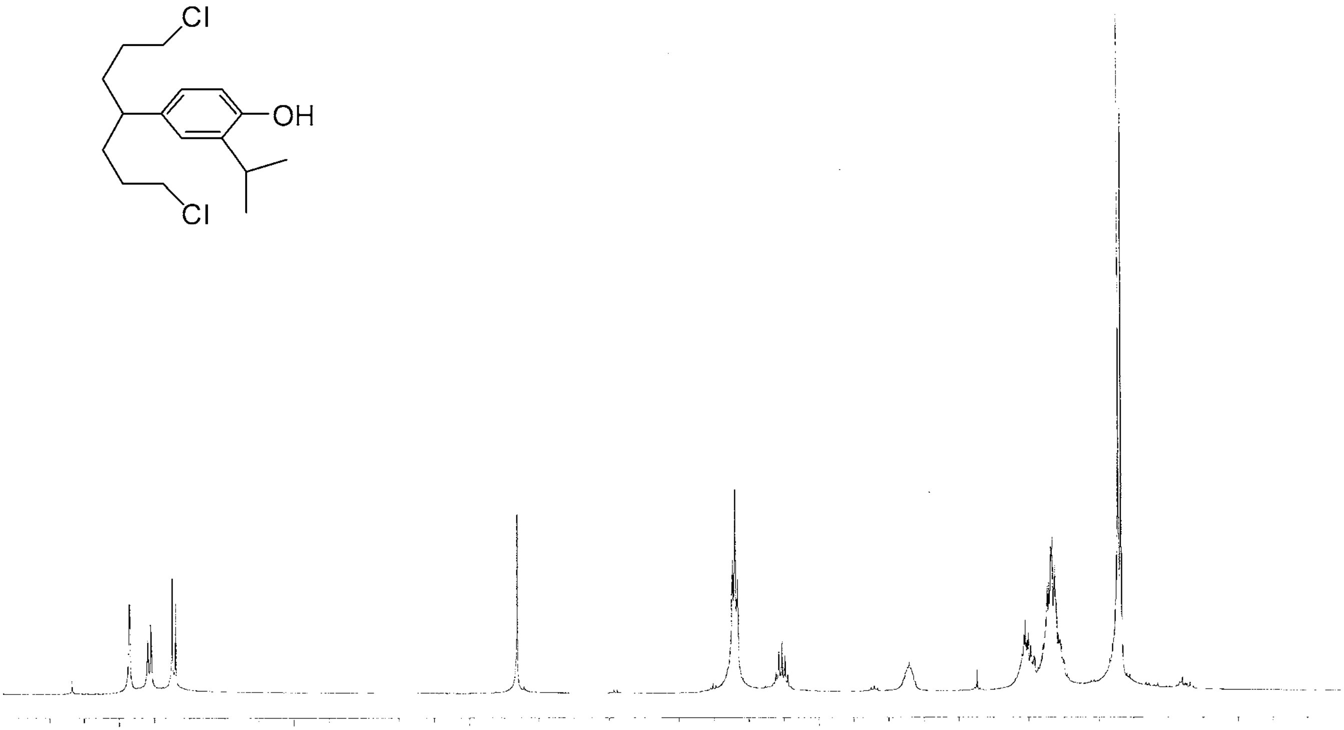
<The ^{1}H NMR spectrum (CDCl$_3$, 25°C) of **27**>


Cl
OH
Cl
EA
EA
EA
7
6
5
4
3
2
1
ppm

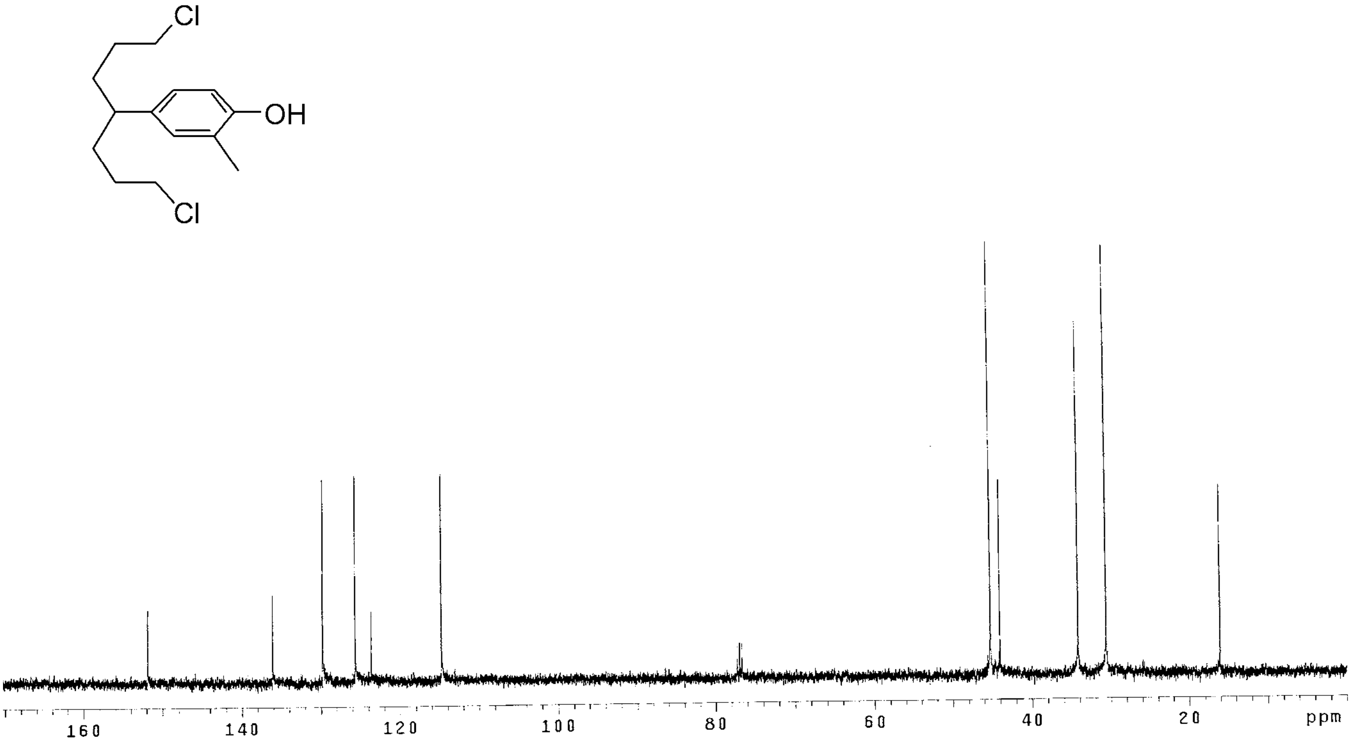
<The ^{13}C NMR spectrum (CDCl$_3$, 25°C) of **28**>


Cl
OH
Cl
160
140
120
100
80
60
40
20
ppm

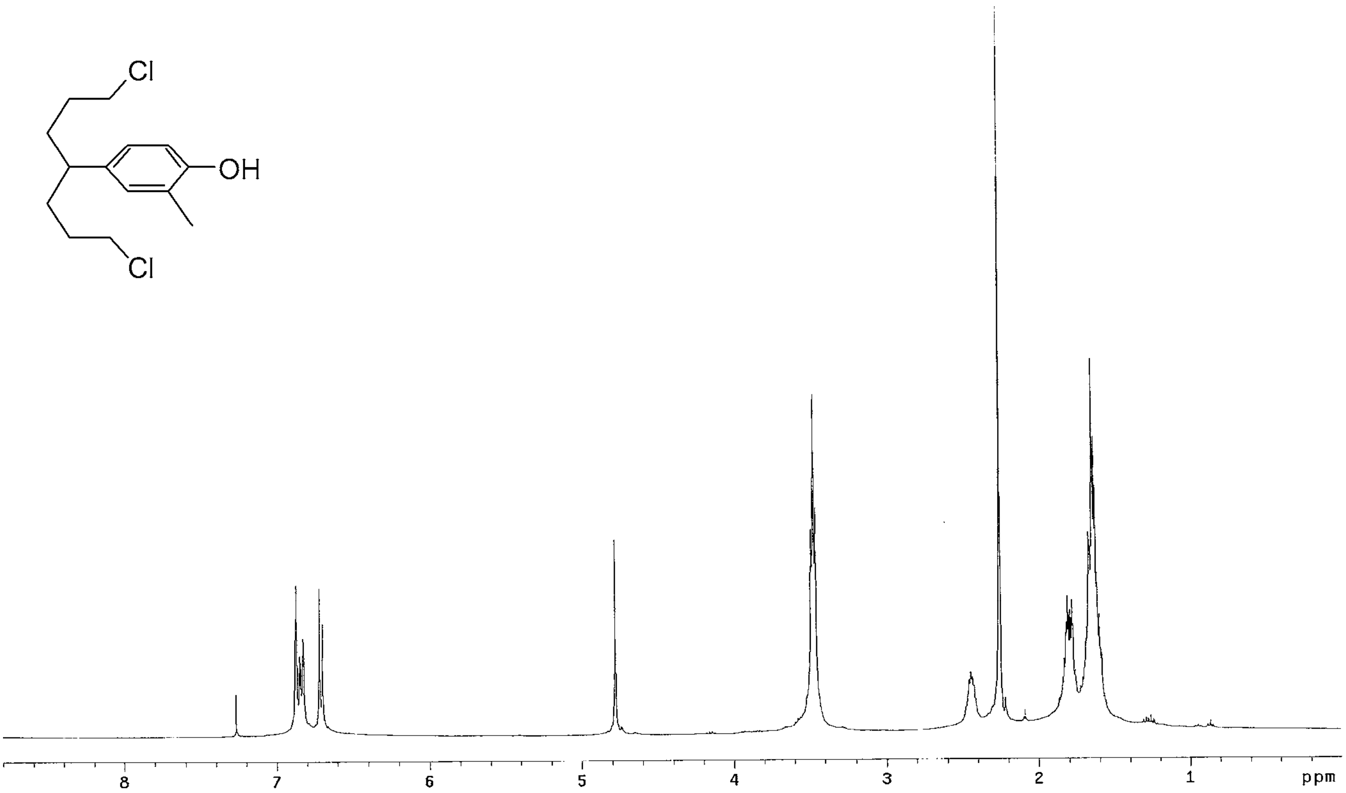
<The ^{1}H NMR NMR spectrum (CDCl$_3$, 25°C) of **28**>


Cl
OH
Cl
7
6
5
4
3
2
1
ppm

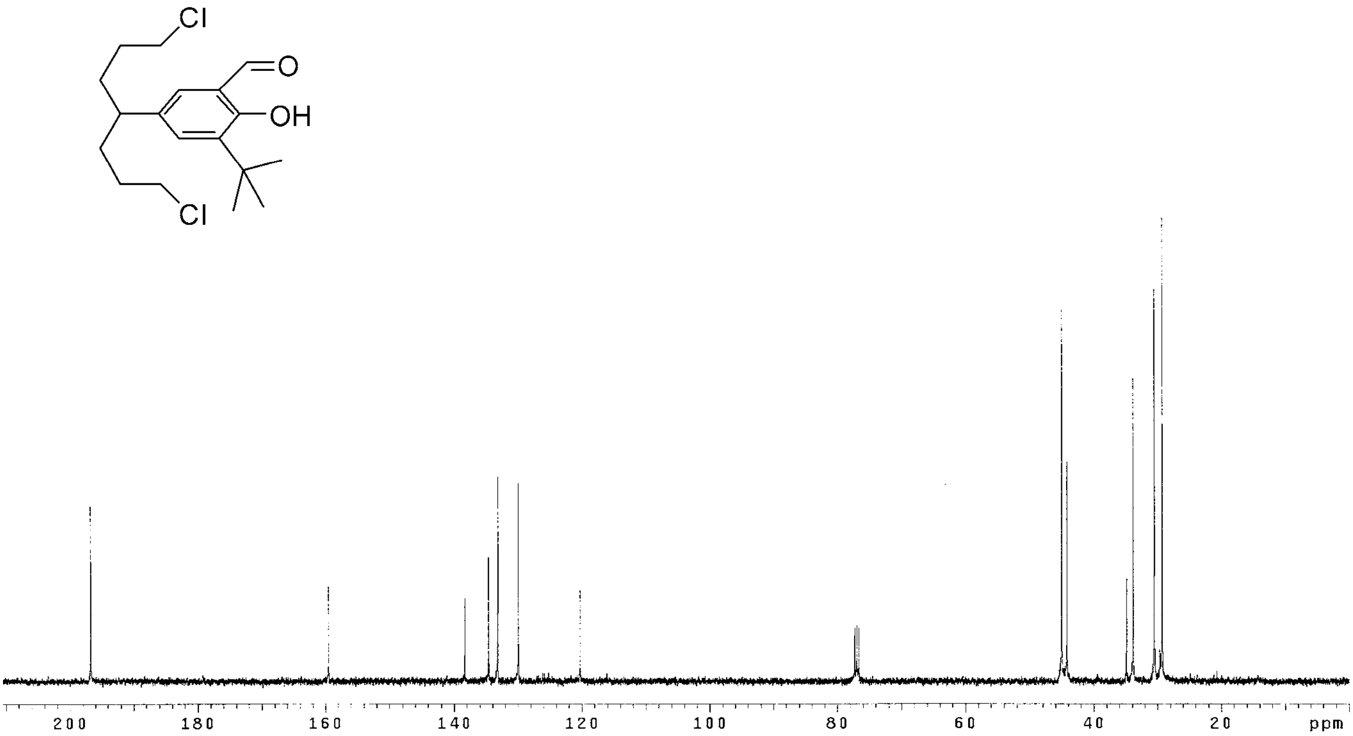
<The ^{13}C NMR spectrum (CDCl$_3$, 25^{o}C) of **29**>


Cl
OH
Cl
160
140
120
100
80
60
40
20
ppm

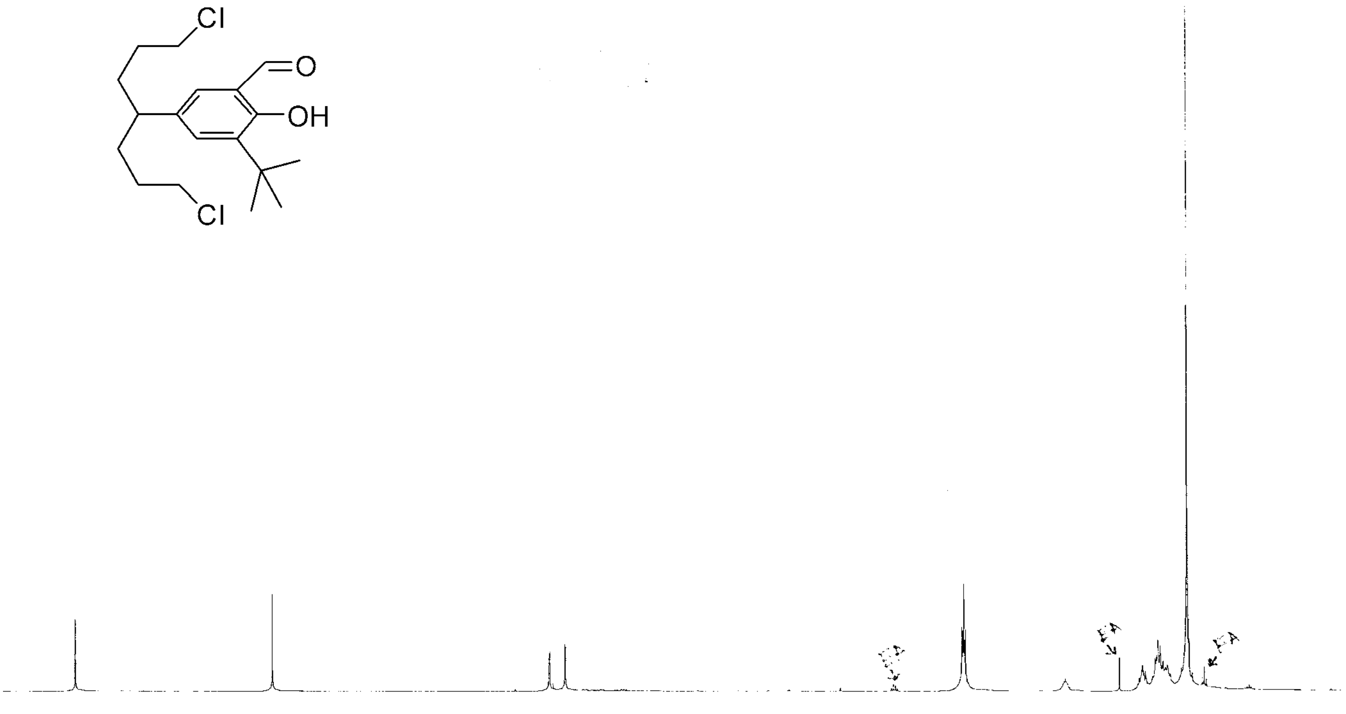
<The ^{1}H NMR spectrum (CDCl$_3$, 25^{o}C) of **29**>


Cl
OH
Cl
8
7
6
5
4
3
2
1
ppm

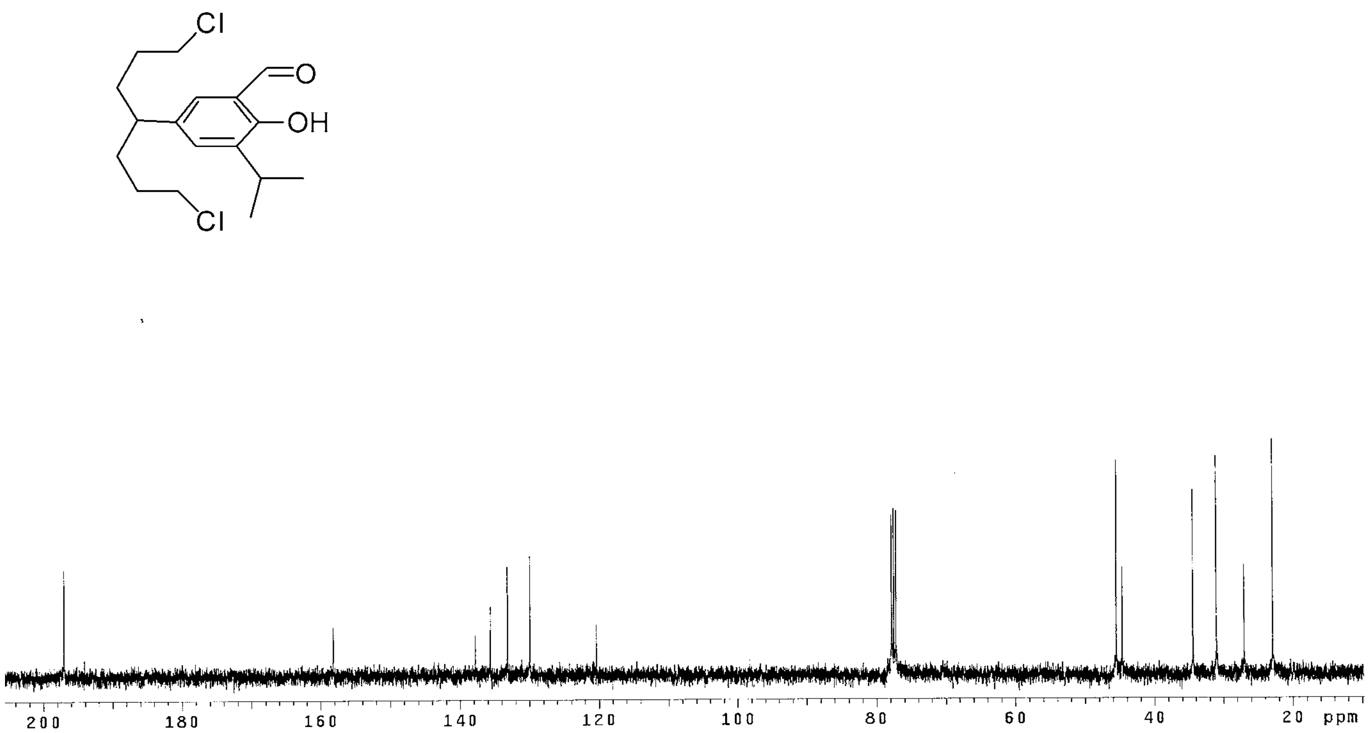
<The ^{13}C NMR spectrum ($CDCl_3$, 25°C) of **30**>


Cl
O
OH
Cl
200
180
160
140
120
100
80
60
40
20
ppm

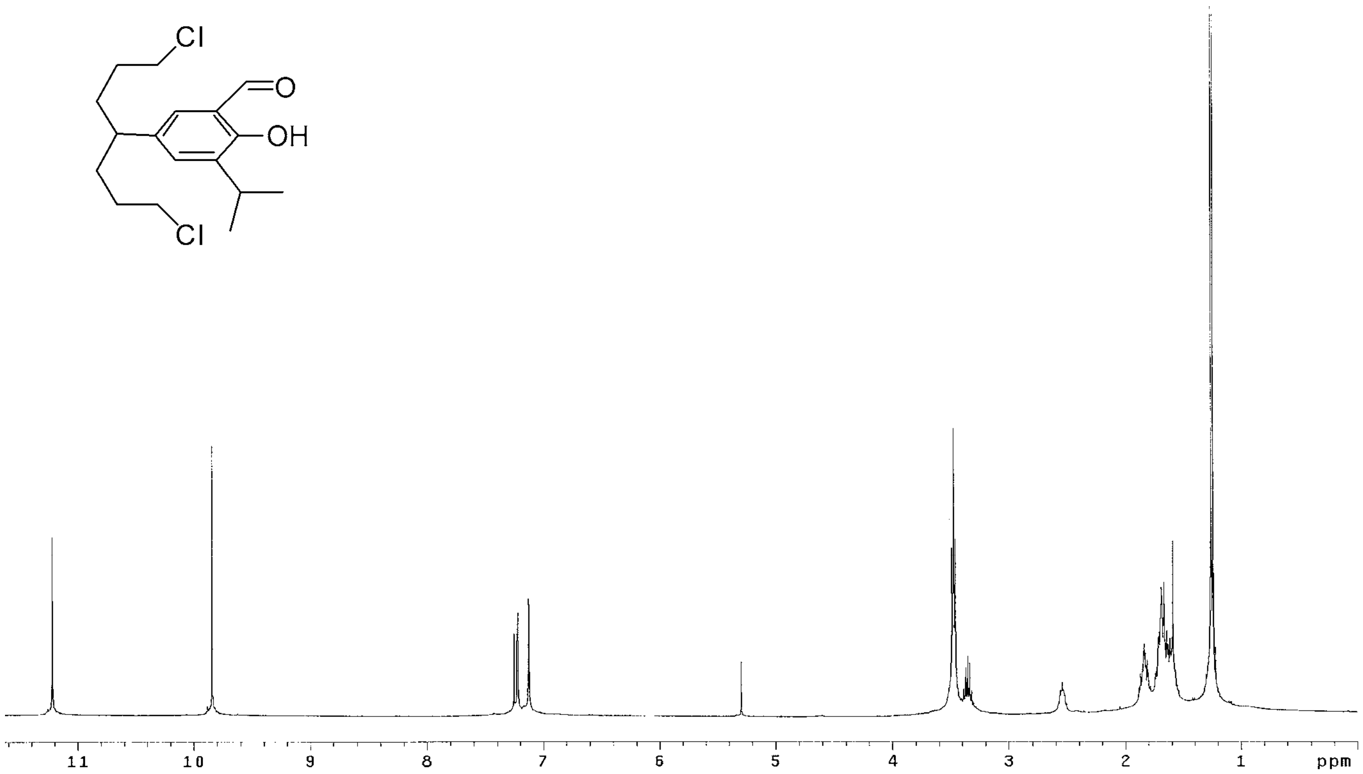
<The ^{1}H spectrum ($CDCl_3$, 25°C) of **30**>


Cl
O
OH
Cl
12
11
10
9
8
7
6
5
4
3
2
1
ppm

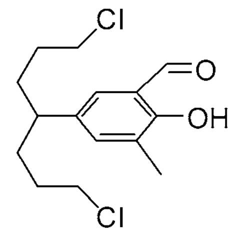
<The ^{13}C NMR spectrum ($CDCl_3$, 25°C) of **31**>

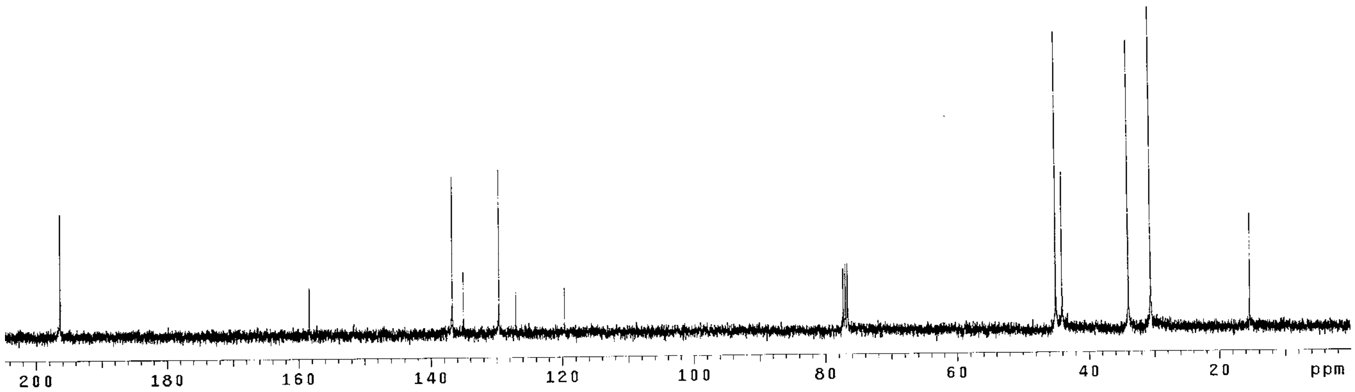

Cl
O
OH
Cl
200
180
160
140
120
100
80
60
40
20
ppm

<The ^{1}H NMR spectrum ($CDCl_3$, 25°C) of **31**>

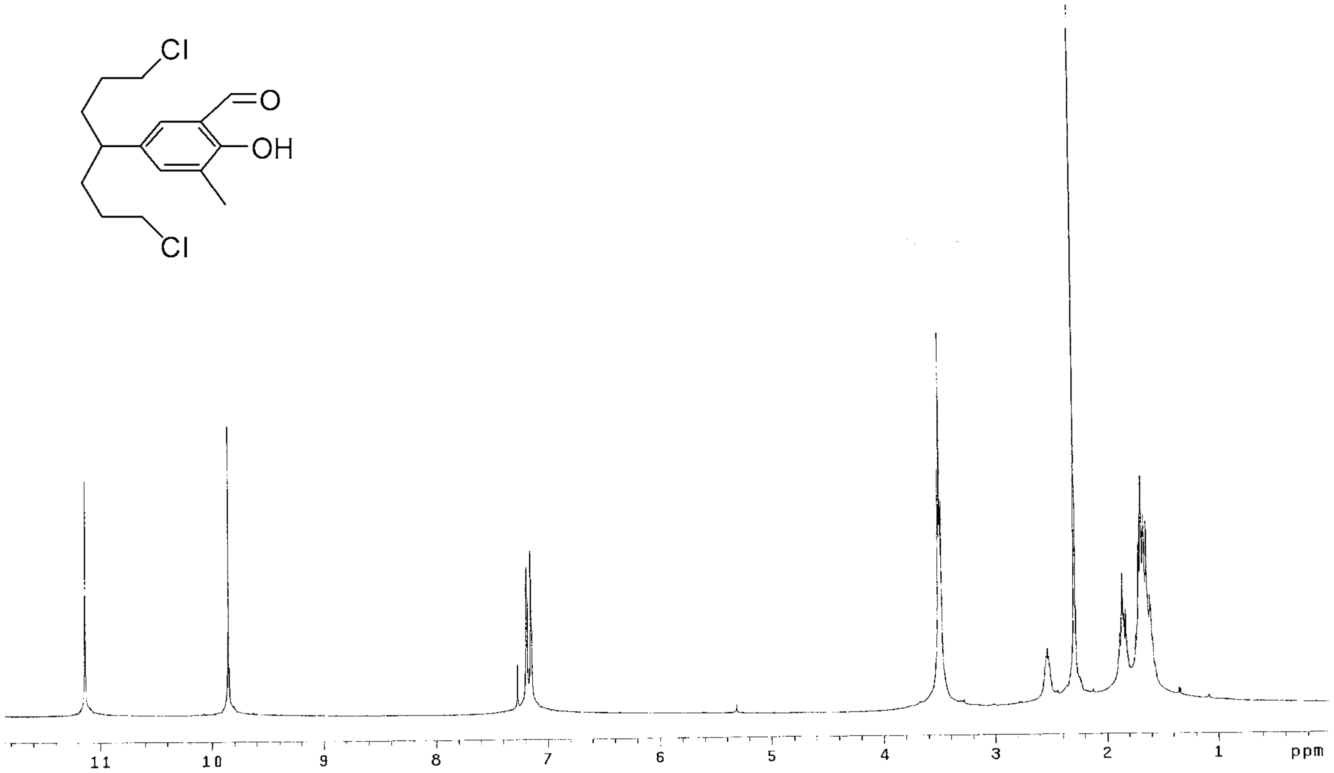

Cl
O
OH
Cl
11
10
9
8
7
6
5
4
3
2
1
ppm

<The ^{13}C NMR spectrum (CDCl$_3$, 25^{o}C) of **32**>


Cl
O
OH
Cl

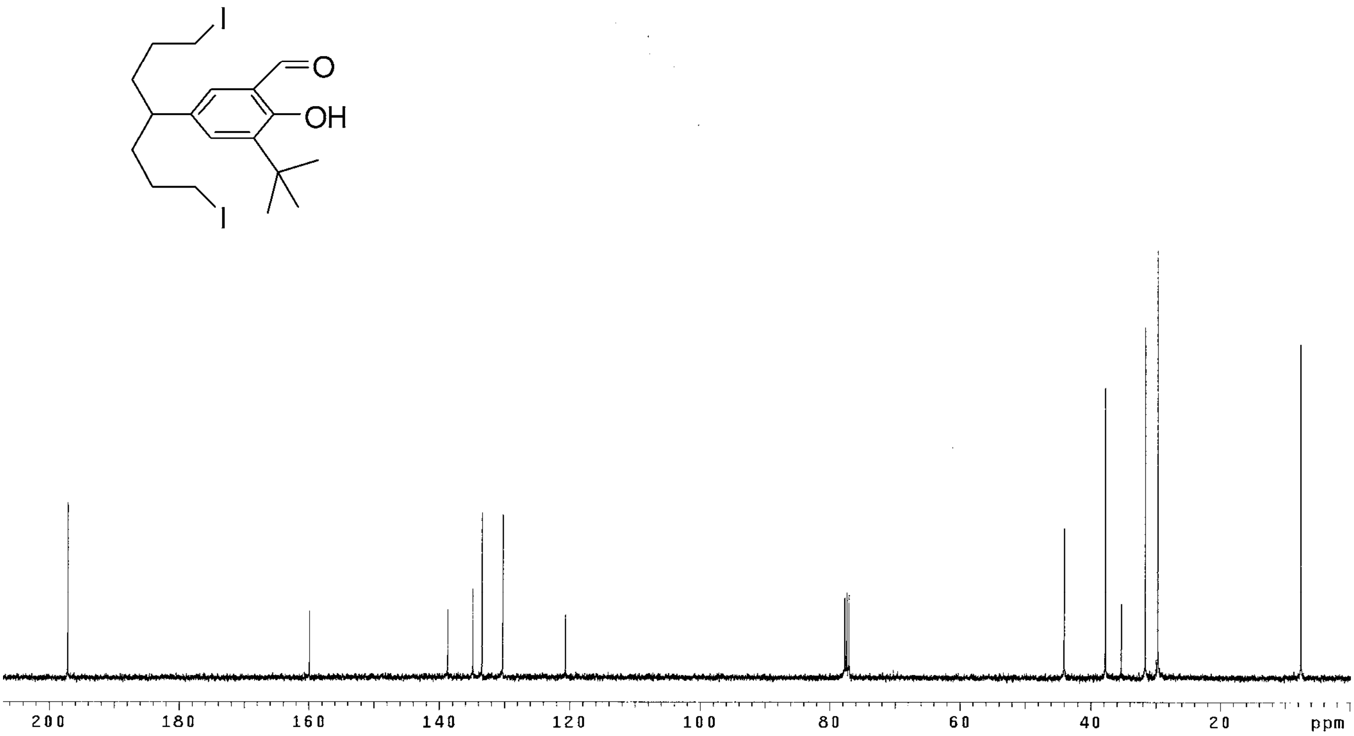

200
180
160
140
120
100
80
60
40
20
ppm

<The ^{1}H NMR spectrum (CDCl$_3$, 25^{o}C) of **32**>


Cl
O
OH
Cl

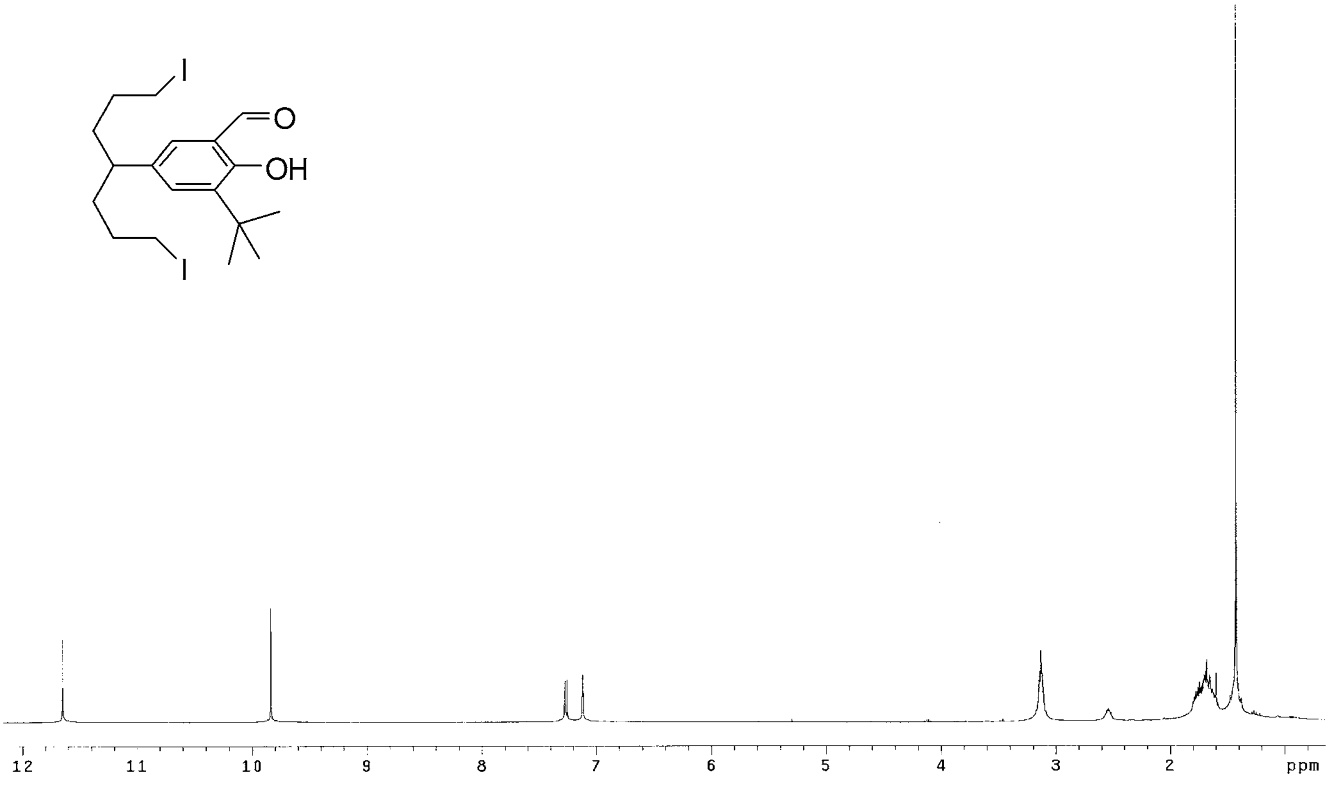
11
10
9
8
7
6
5
4
3
2
1
ppm

<The ^{13}C NMR spectrum ($CDCl_3$, 25°C) of **33**>



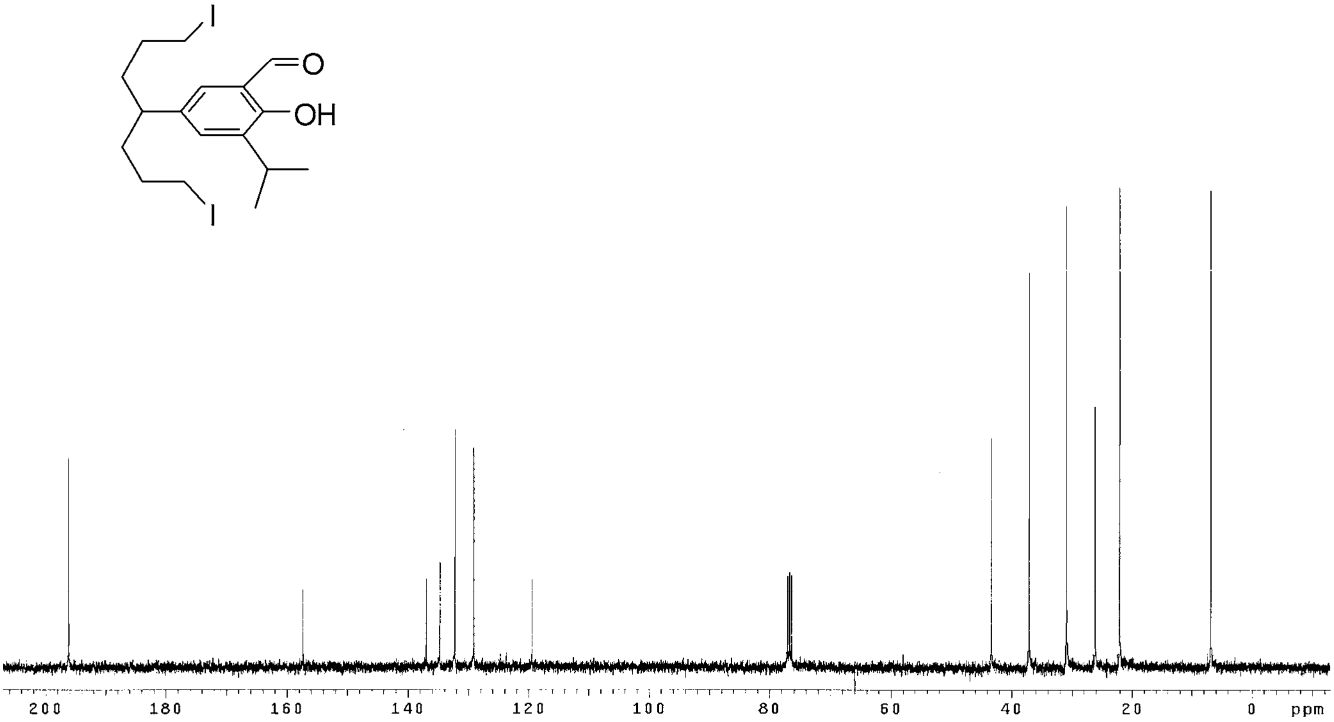
I
O
OH
I
200
180
160
140
120
100
80
60
40
20
ppm

<The ^{1}H NMR spectrum ($CDCl_3$, 25°C) of **33**>

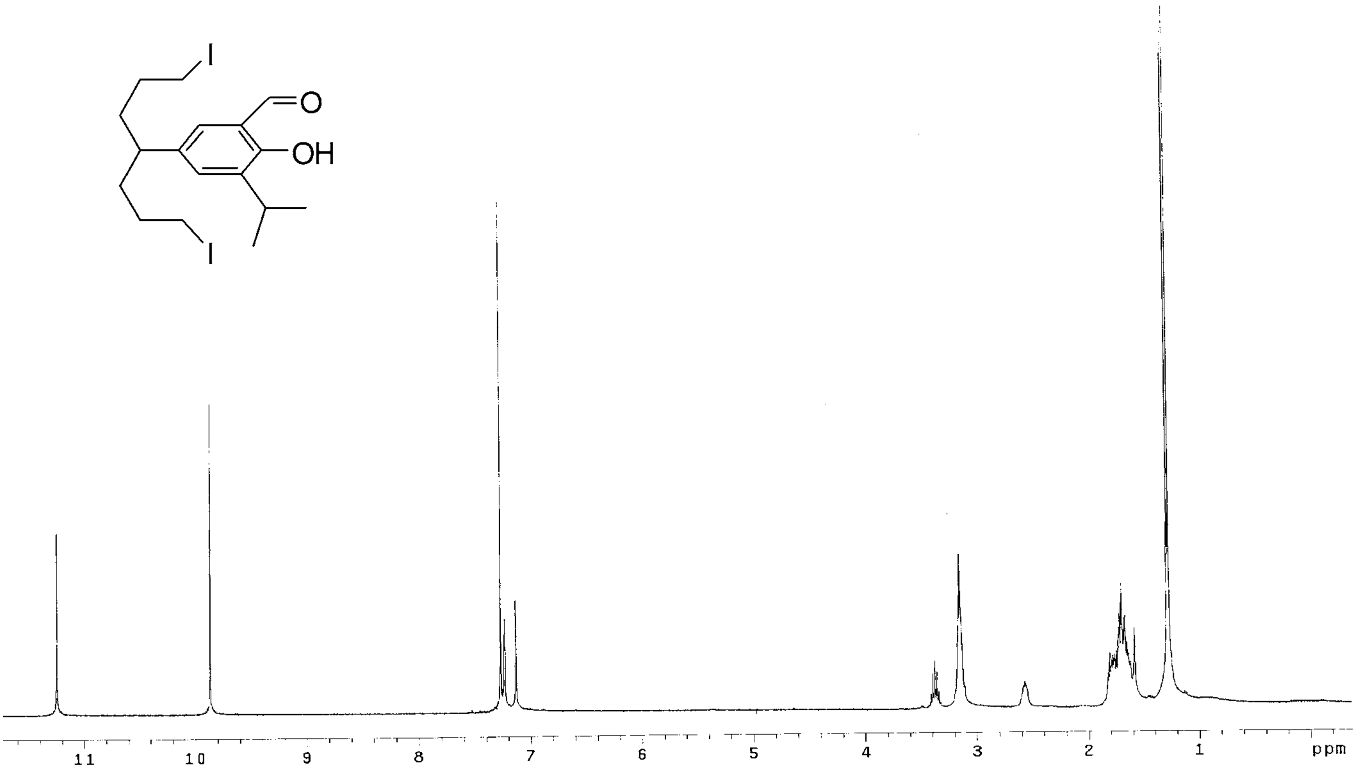


I
O
OH
I
12
11
10
9
8
7
6
5
4
3
2
ppm

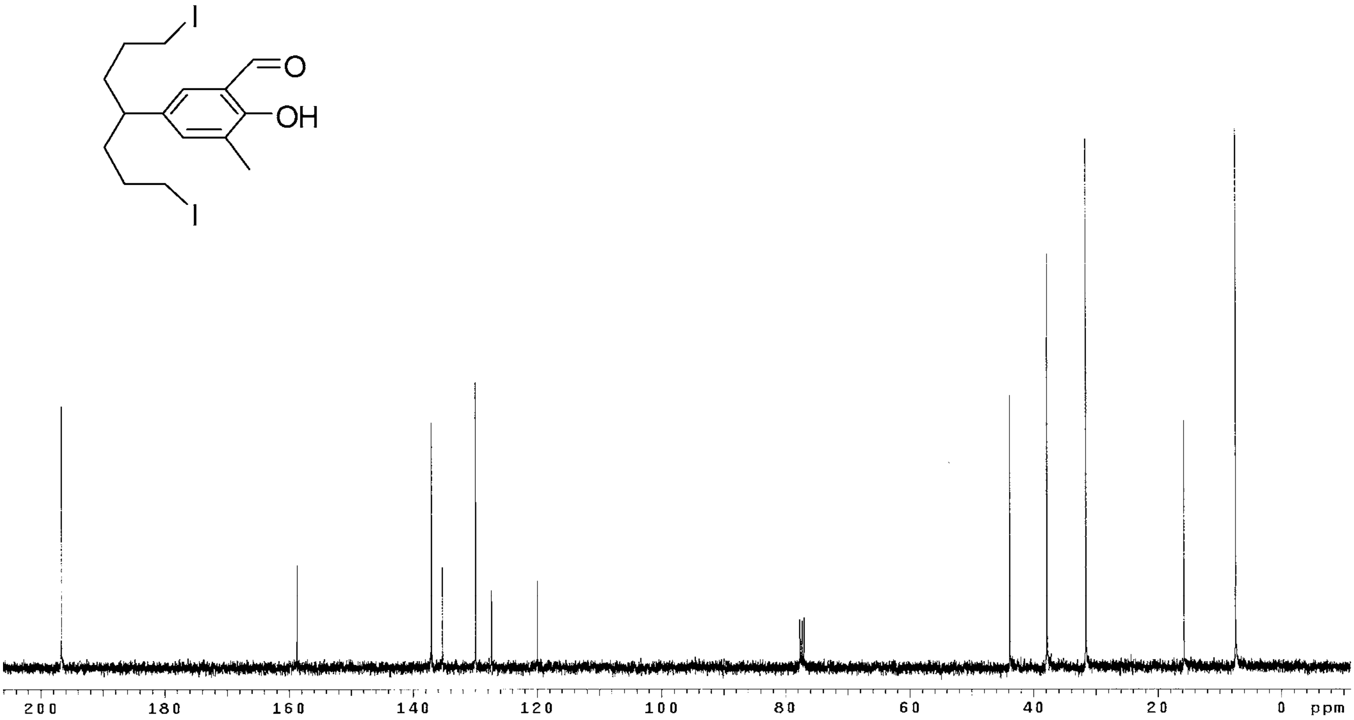
<The ^{13}C NMR spectrum ($CDCl_3$, 25°C) of **34**>


I
O
OH
I
200
180
160
140
120
100
80
60
40
20
0
ppm

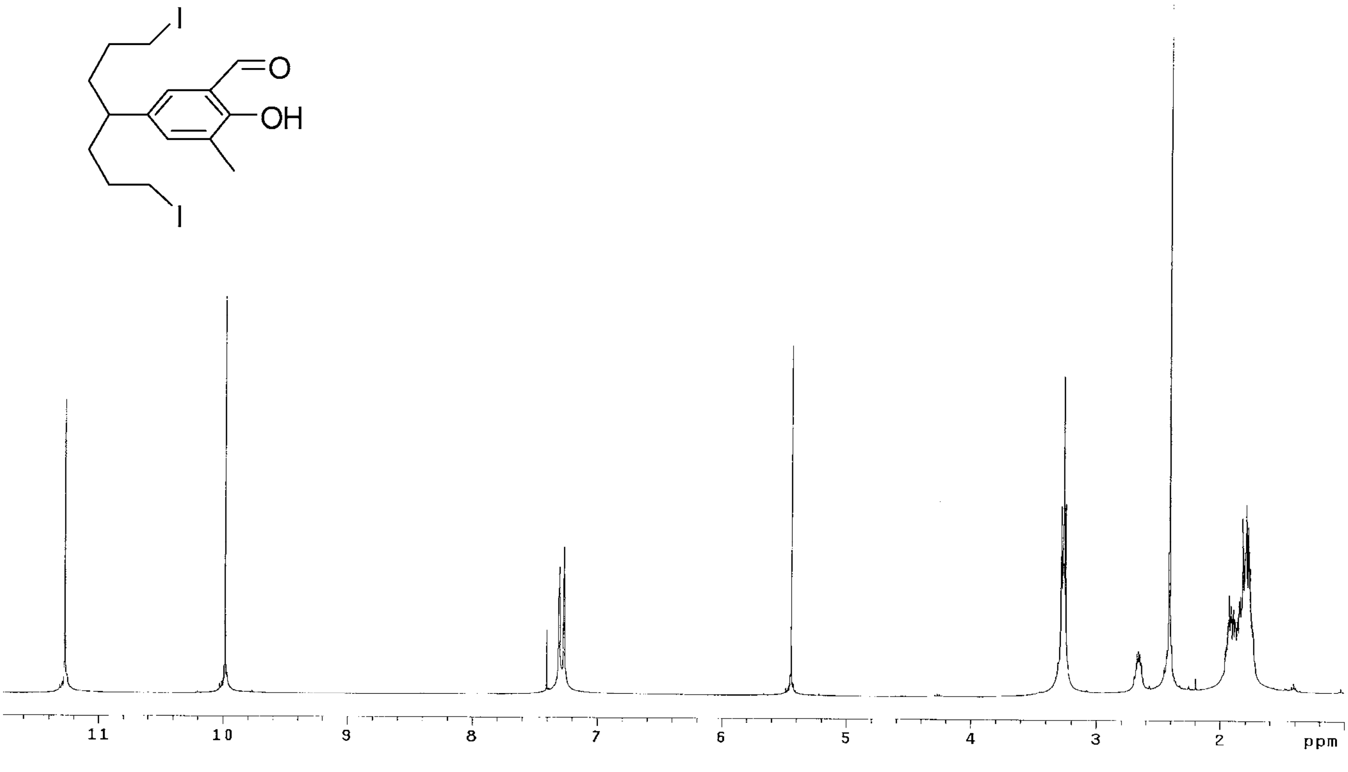
<The ^{1}H NMR spectrum ($CDCl_3$, 25°C) of **34**>


I
O
OH
I
11
10
9
8
7
6
5
4
3
2
1
ppm

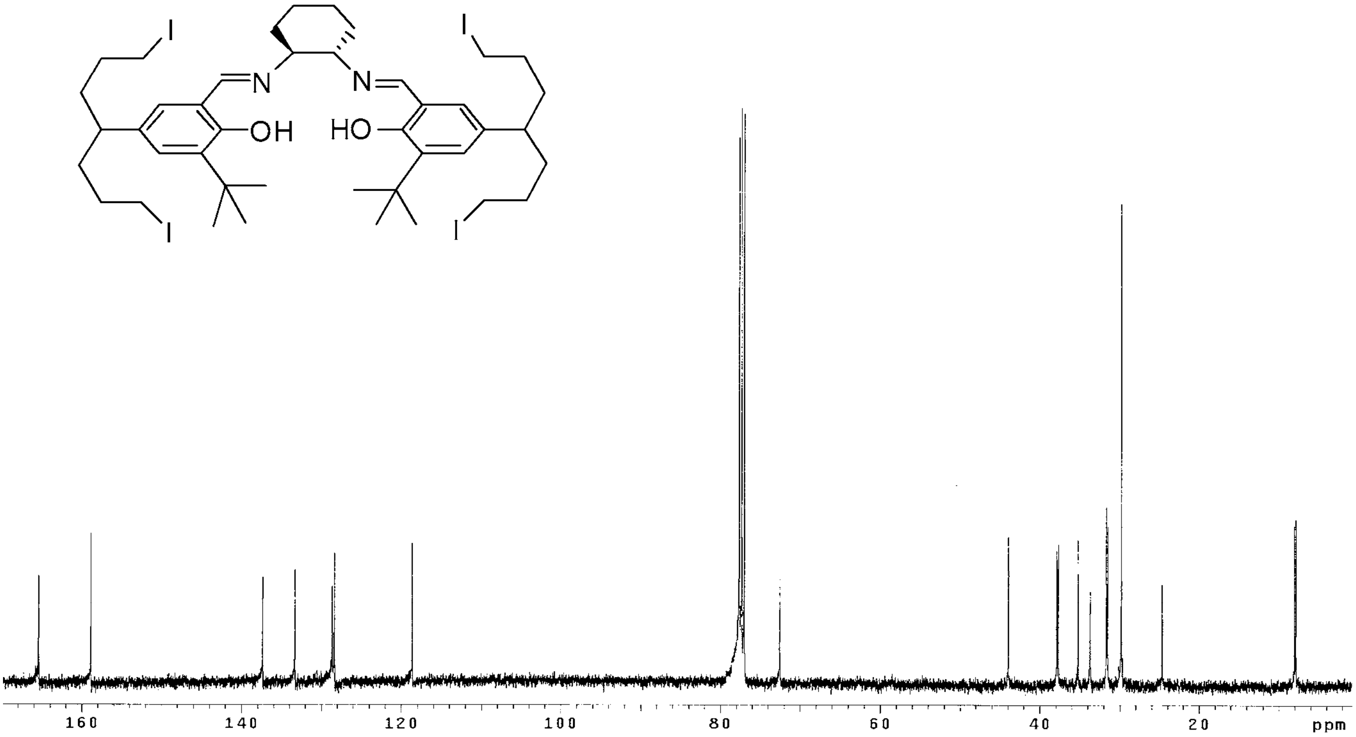
<The ^{13}C NMR spectrum ($CDCl_3$, 25°C) of **35**>


I
O
OH
I
200
180
160
140
120
100
80
60
40
20
0
ppm

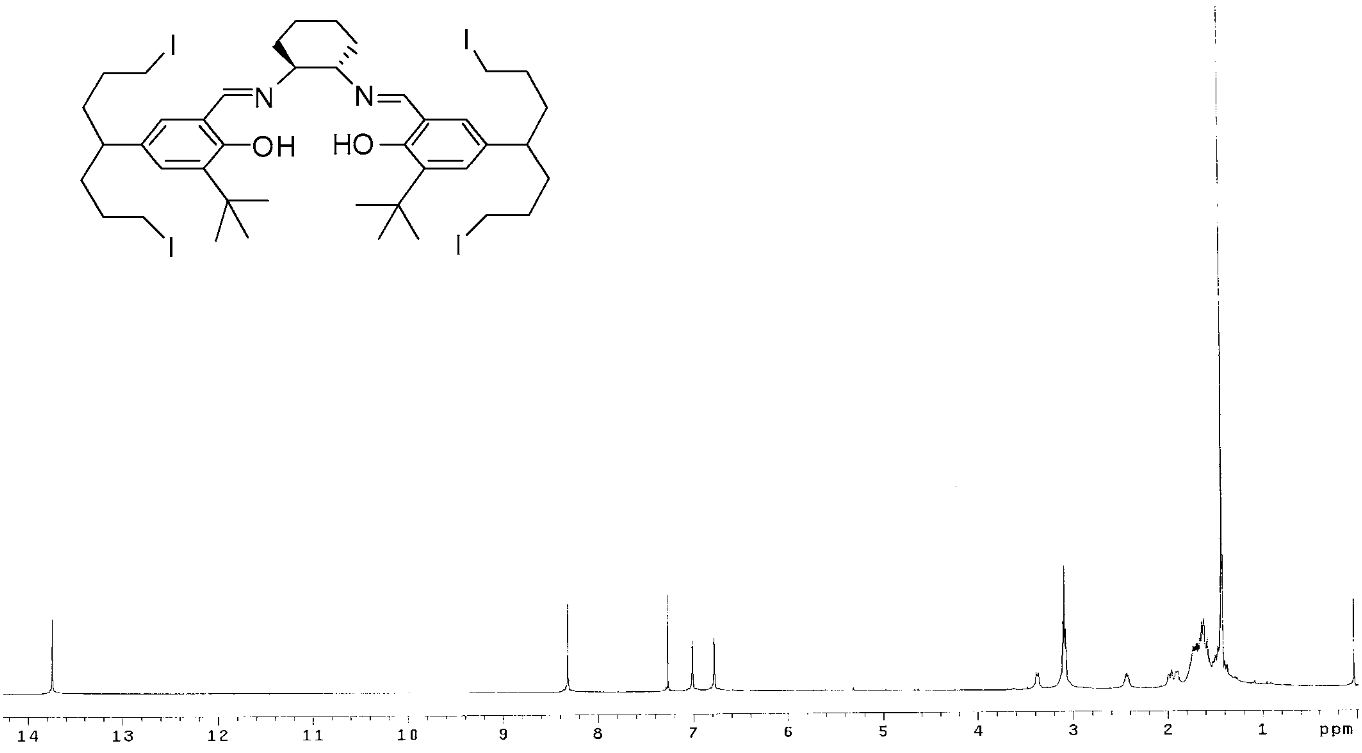
<The ^{1}H NMR spectrum ($CDCl_3$, 25°C) of **35**>


I
O
OH
I
11
10
9
8
7
6
5
4
3
2
ppm

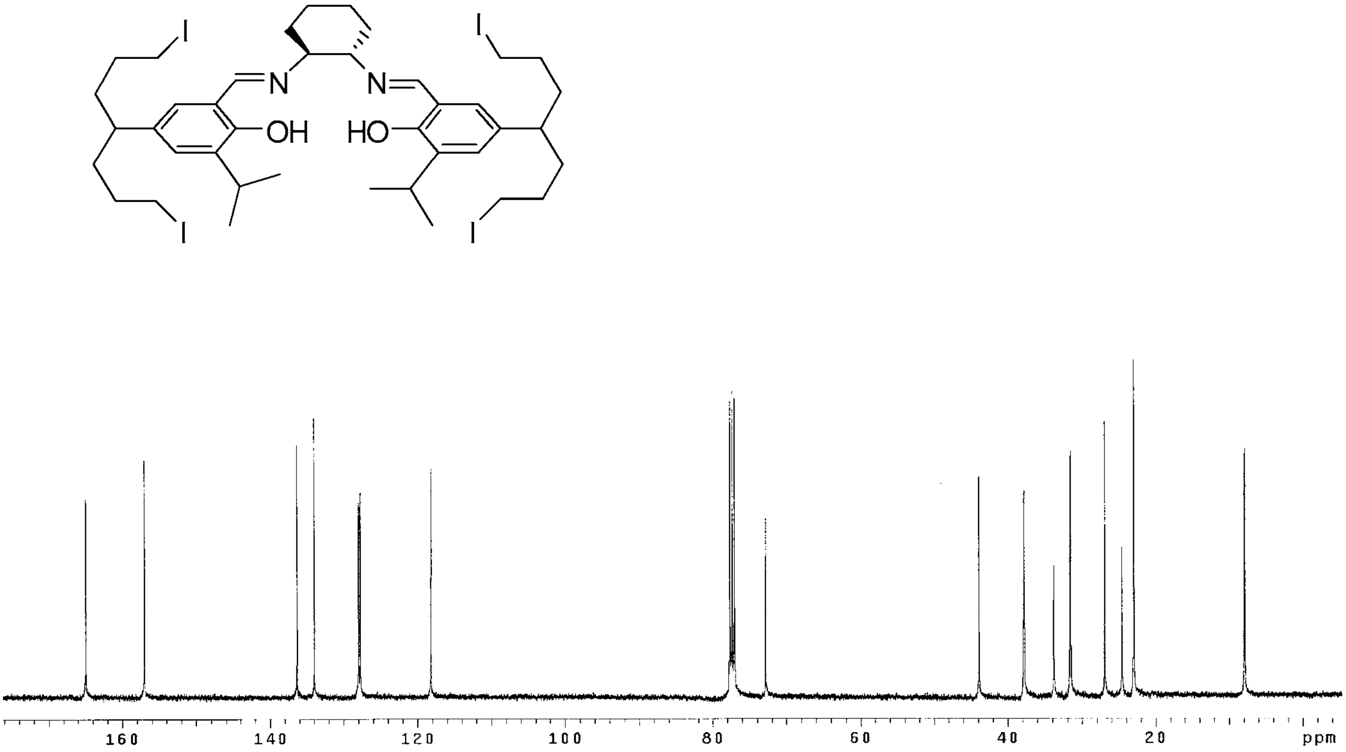
<The ^{13}C NMR spectrum ($CDCl_3$, 25^{o}C) of **36**>


I
I
I
I
N
N
OH
HO
160
140
120
100
80
60
40
20
ppm

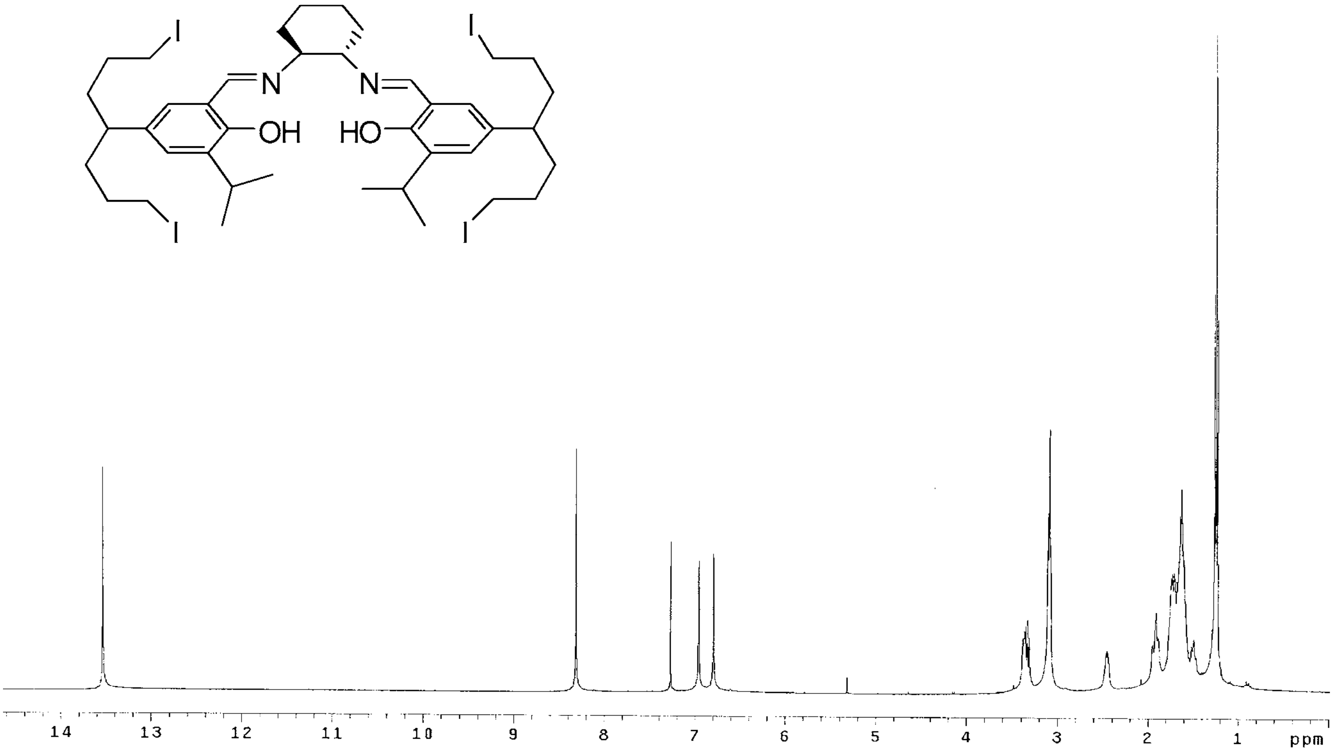
<The ^{1}H NMR spectrum ($CDCl_3$, 25^{o}C) of **36**>


I
I
I
I
N
N
OH
HO
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

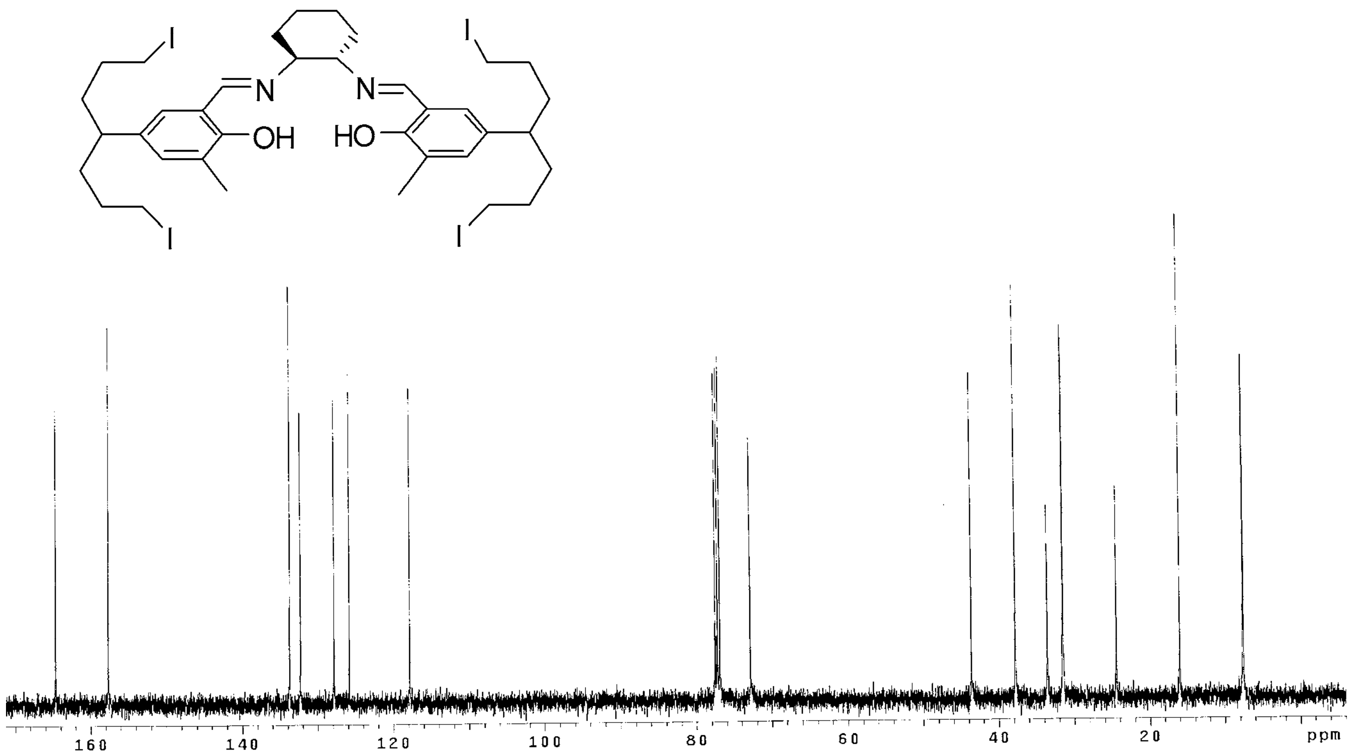
<The ^{13}C NMR spectrum (CDCl$_3$, 25^{o}C) of **37**>


I
N
N
OH
HO
I
I
I
160
140
120
100
80
60
40
20
ppm

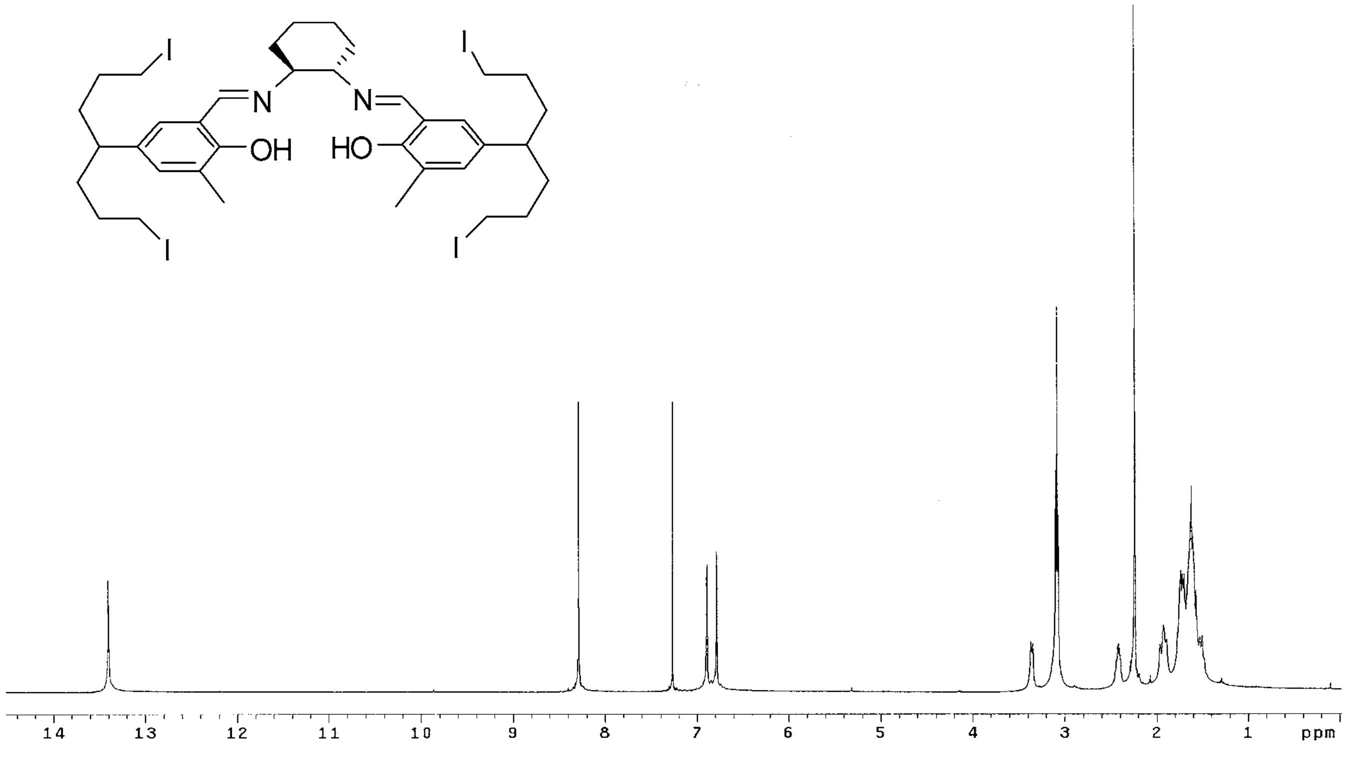
<The ^{1}H NMR spectrum (CDCl$_3$, 25^{o}C) of **37**>


I
N
N
OH
HO
I
I
I
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

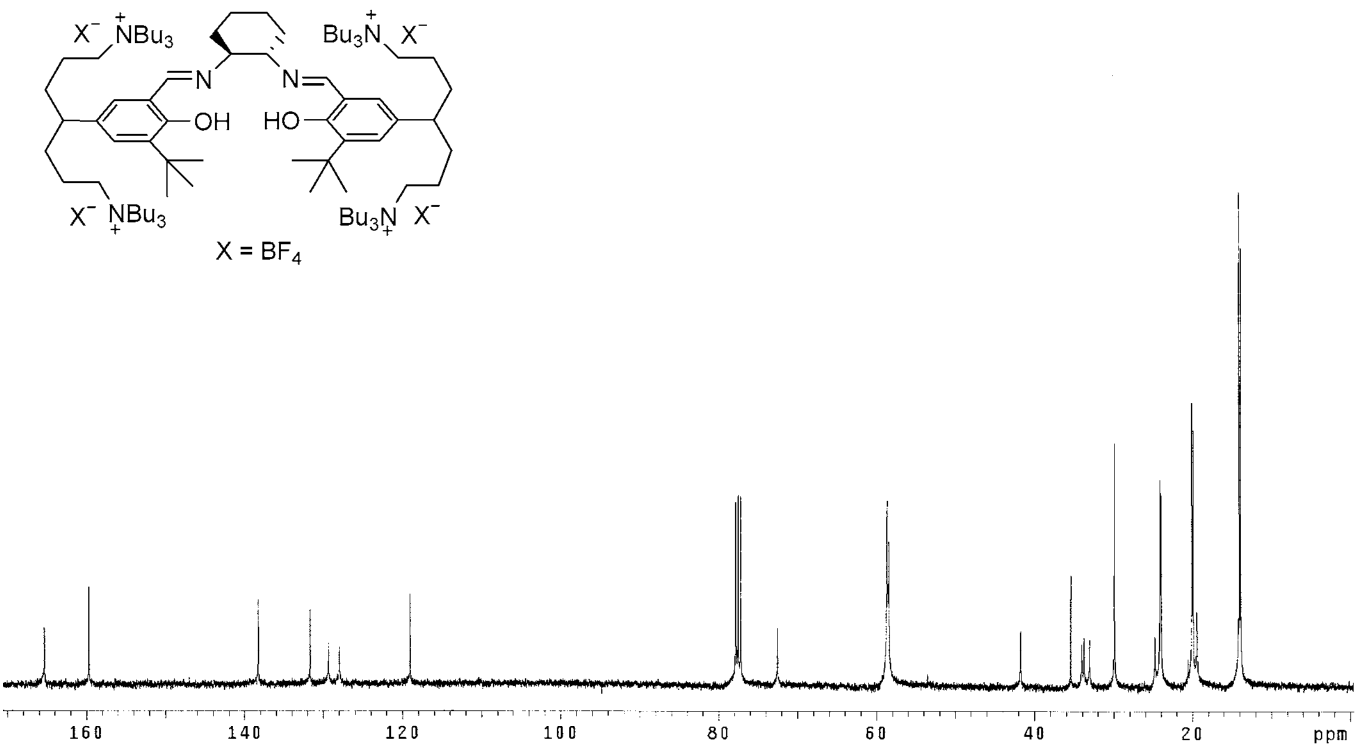
<The ^{13}C NMR spectrum ($CDCl_3$, 25°C) of **38**>


I
I
N
N
OH
HO
I
I
160
140
120
100
80
60
40
20
ppm

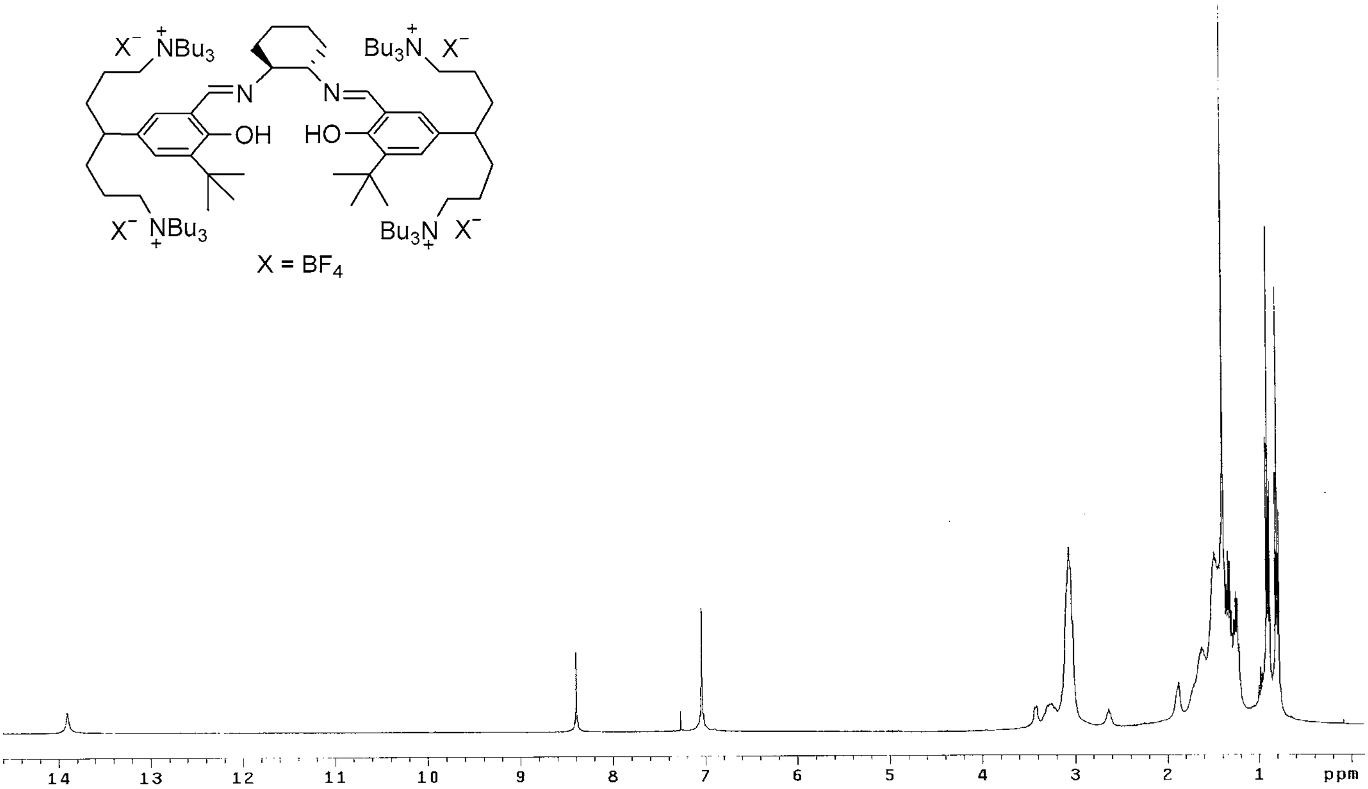
<The ^{1}H NMR spectrum ($CDCl_3$, 25°C) of **38**>


I
I
N
N
OH
HO
I
I
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

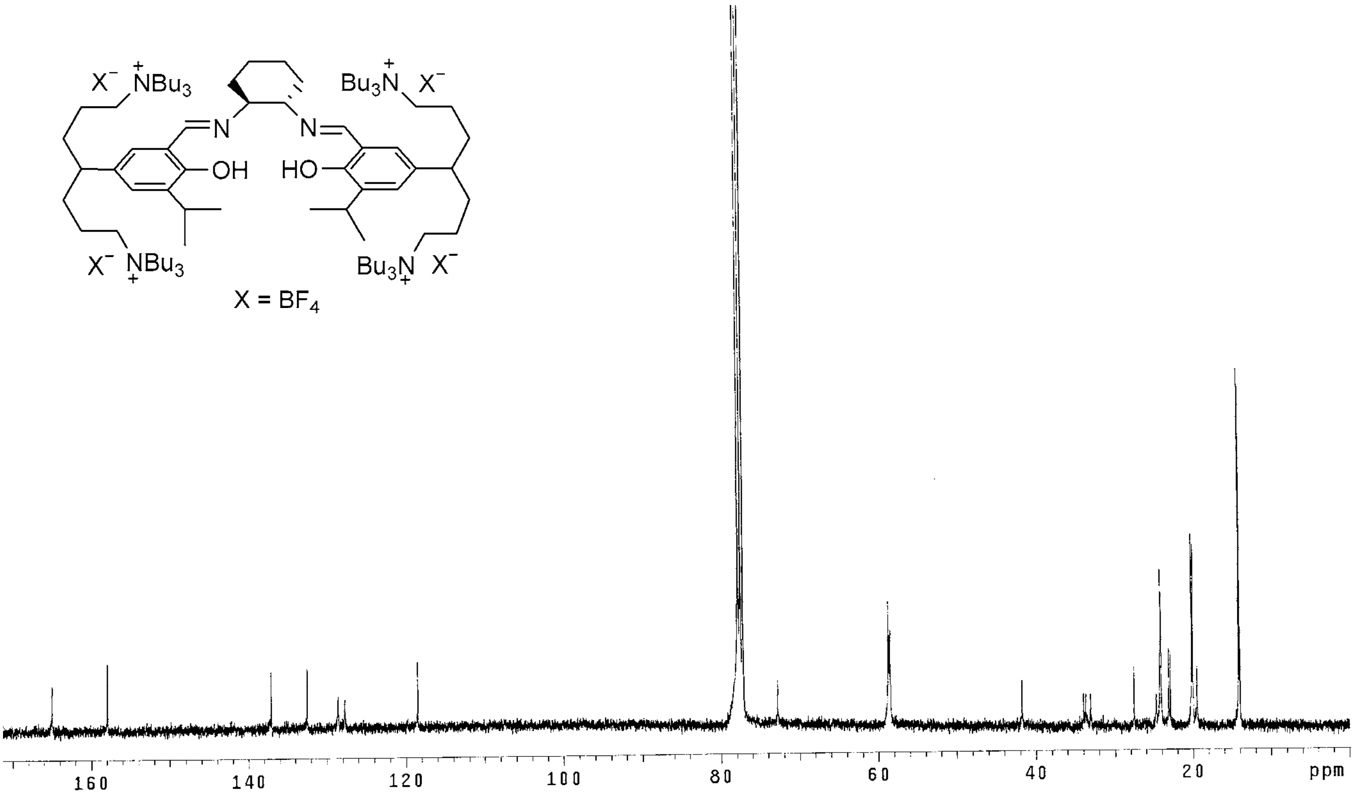
<The ^{13}C NMR spectrum (CDCl$_3$, 25^{o}C) of **39**>


X = BF4
160
140
120
100
80
60
40
20
ppm

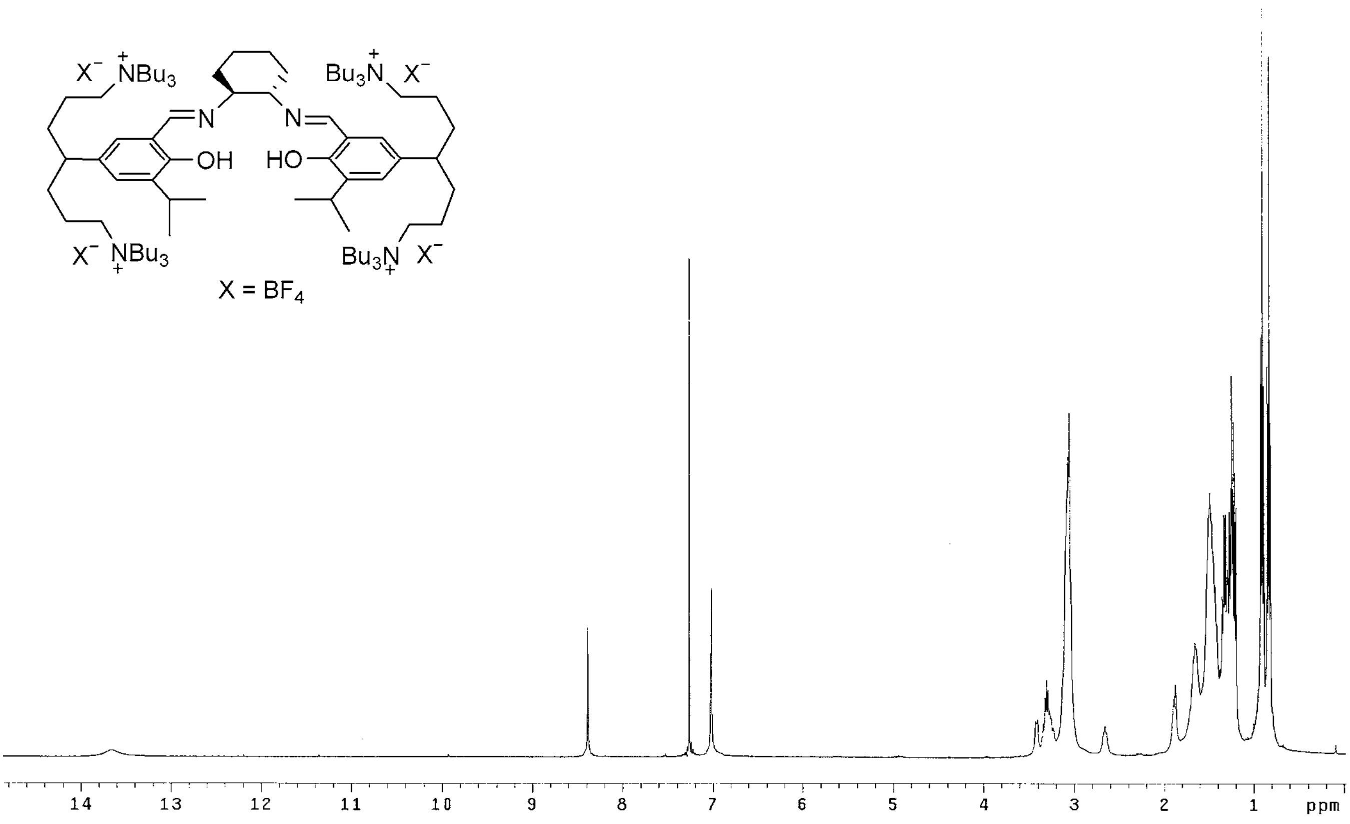
<The ^{1}H NMR spectrum (CDCl$_3$, 25^{o}C) of **39**>


X = BF4
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

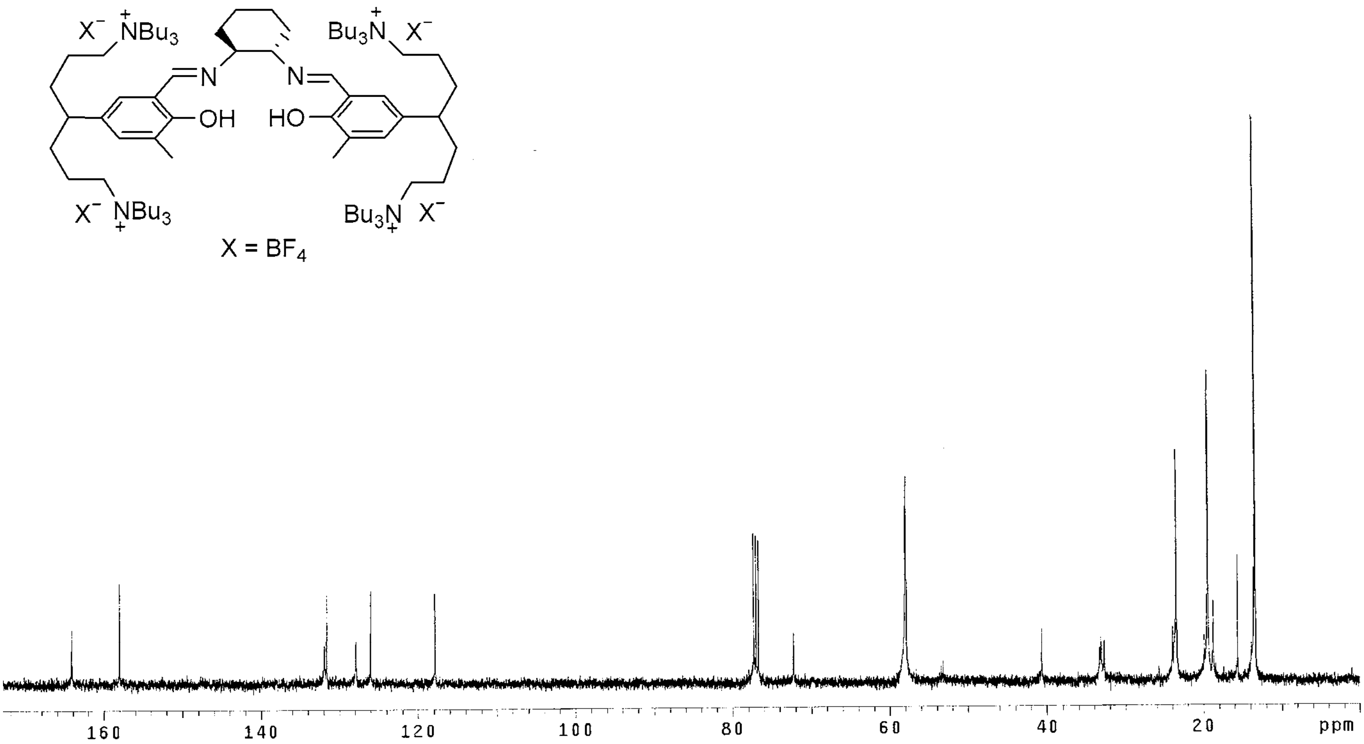
<The ^{13}C NMR spectrum ($CDCl_3$, 25°C) of **40**>


X⁻ NBu3
Bu3N X⁻
N
N
OH
HO
X⁻ NBu3
Bu3N X⁻
X = BF4
160
140
120
100
80
60
40
20
ppm

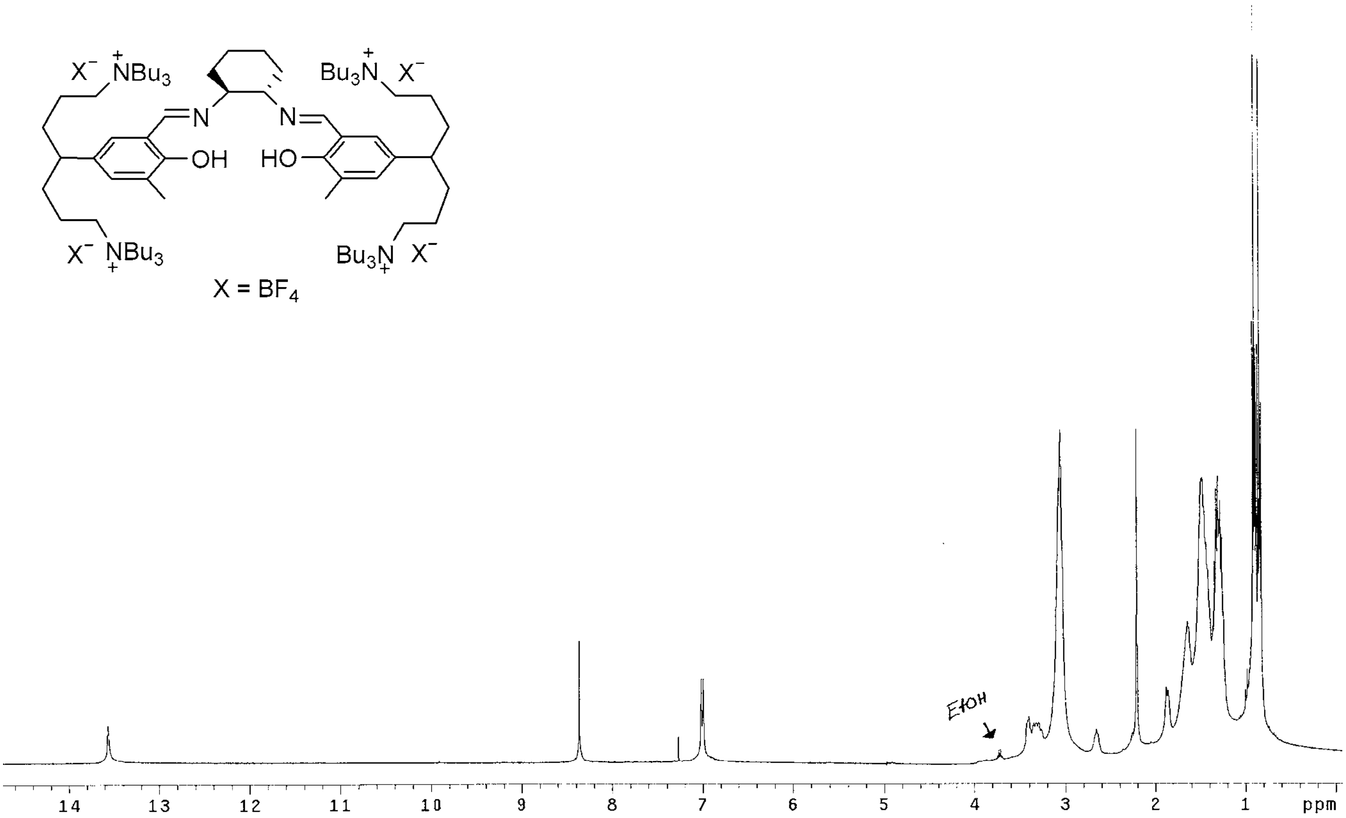
<The ^{1}H NMR spectrum ($CDCl_3$, 25°C) of **40**>


X⁻ NBu3
Bu3N X⁻
N
N
OH
HO
X⁻ NBu3
Bu3N X⁻
X = BF4
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

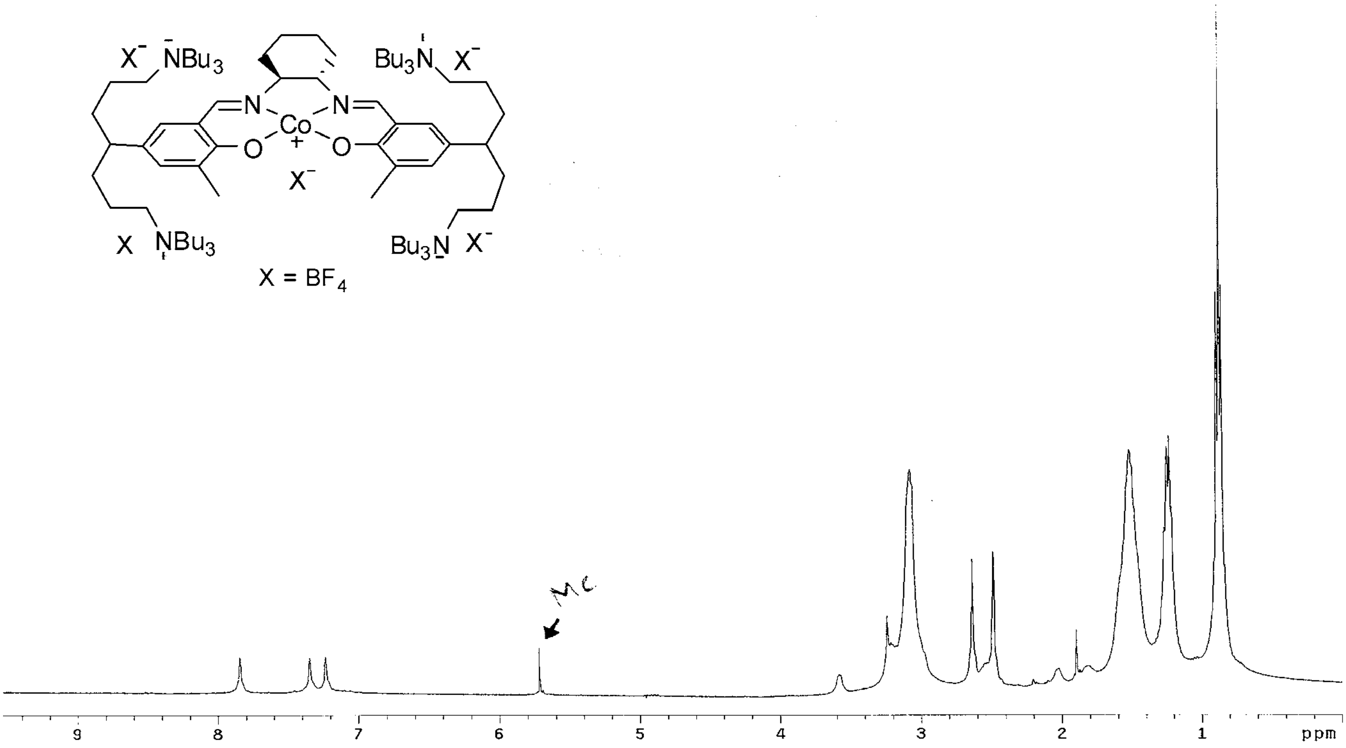
<The ^{13}C NMR spectrum (CDCl$_3$, 25^{o}C) of **41**>


X = BF4
160
140
120
100
80
60
40
20
ppm

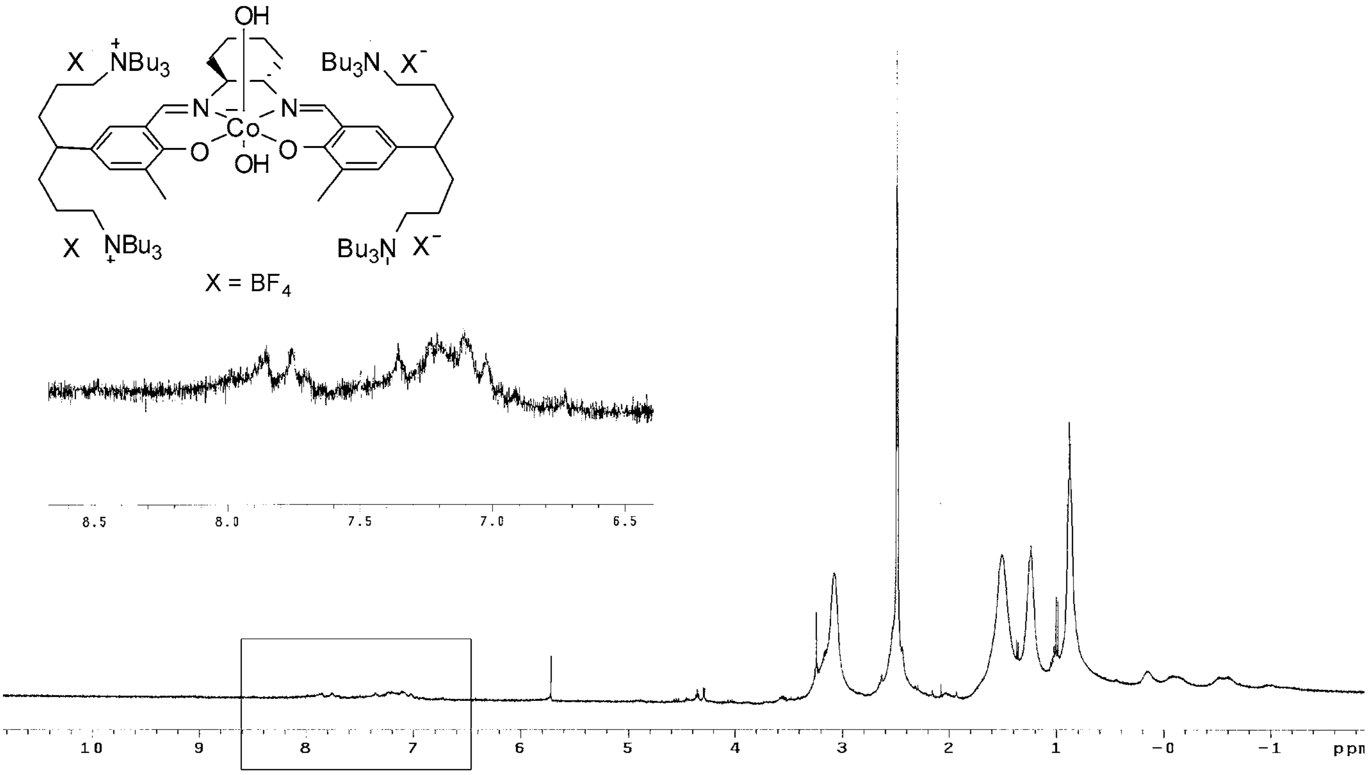
<The ^{1}H NMR spectrum (CDCl$_3$, 25^{o}C) of **41**>


X = BF4
EtOH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

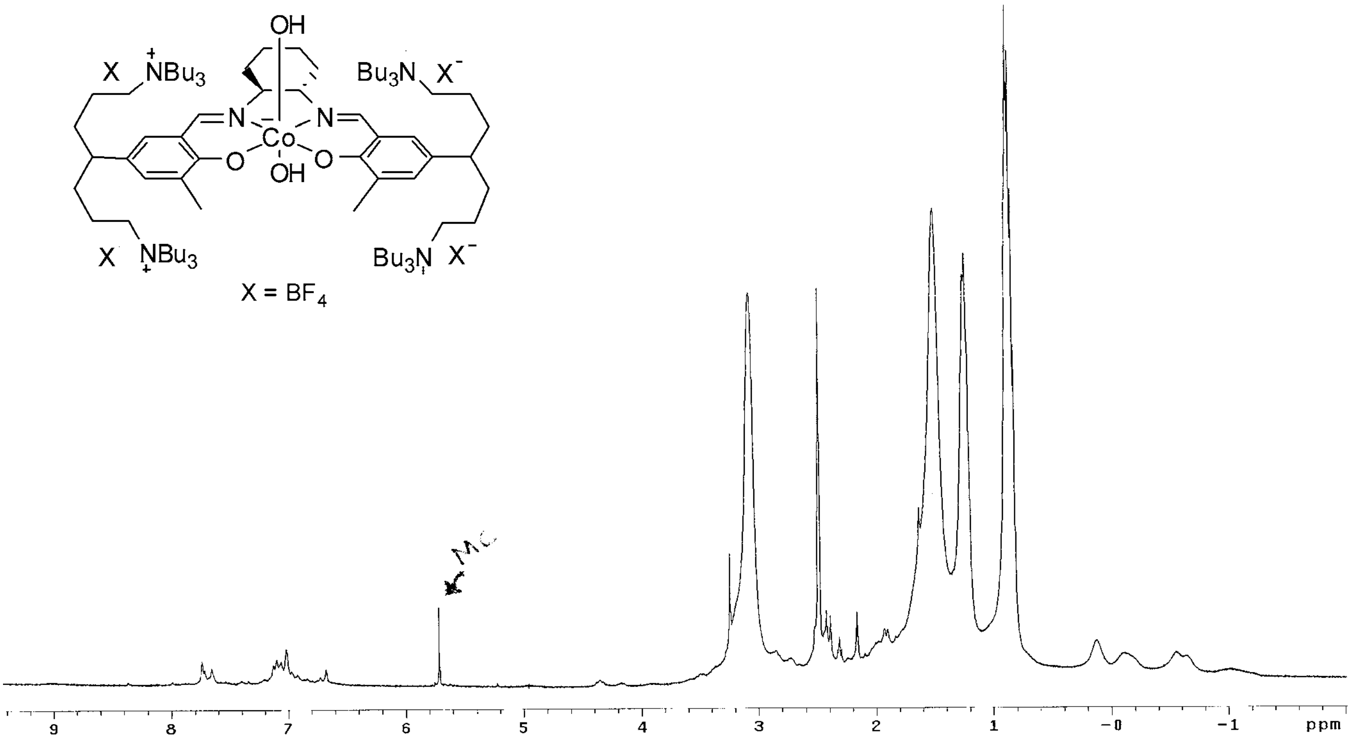
<The ^{1}H NMR spectrum (dmso-d_6, 38°C) of **8** (X = BF_4) complex>


X⁻ NBu3
Bu3N X⁻
N
N
Co
+
O
O
X⁻
X NBu3
Bu3N X⁻
X = BF4
Me
9
8
7
6
5
4
3
2
1
ppm

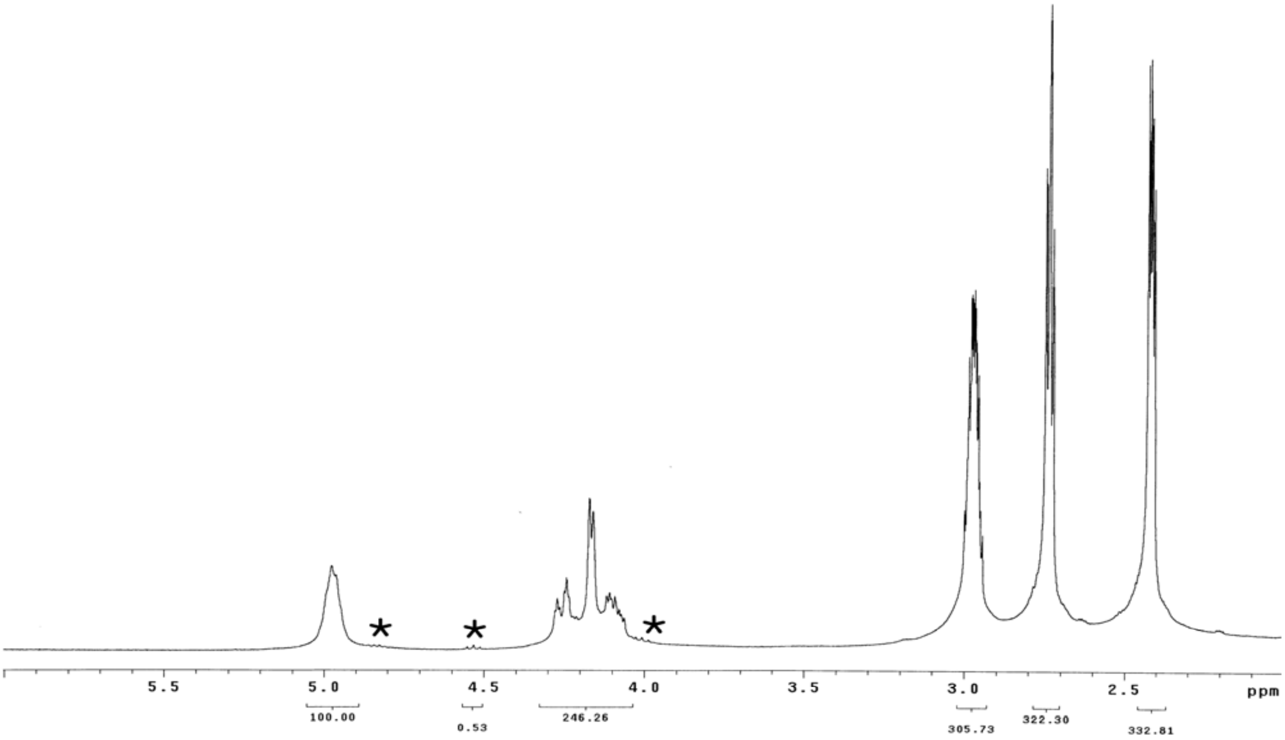
<The ^{1}H NMR spectrum (dmso-d$_6$, 38^{o}C) of the recovered dihydroxylato complex>


OH
X
NBu3
Bu3N
X-
N
Co
O
OH
X = BF4
8.5
8.0
7.5
7.0
6.5
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

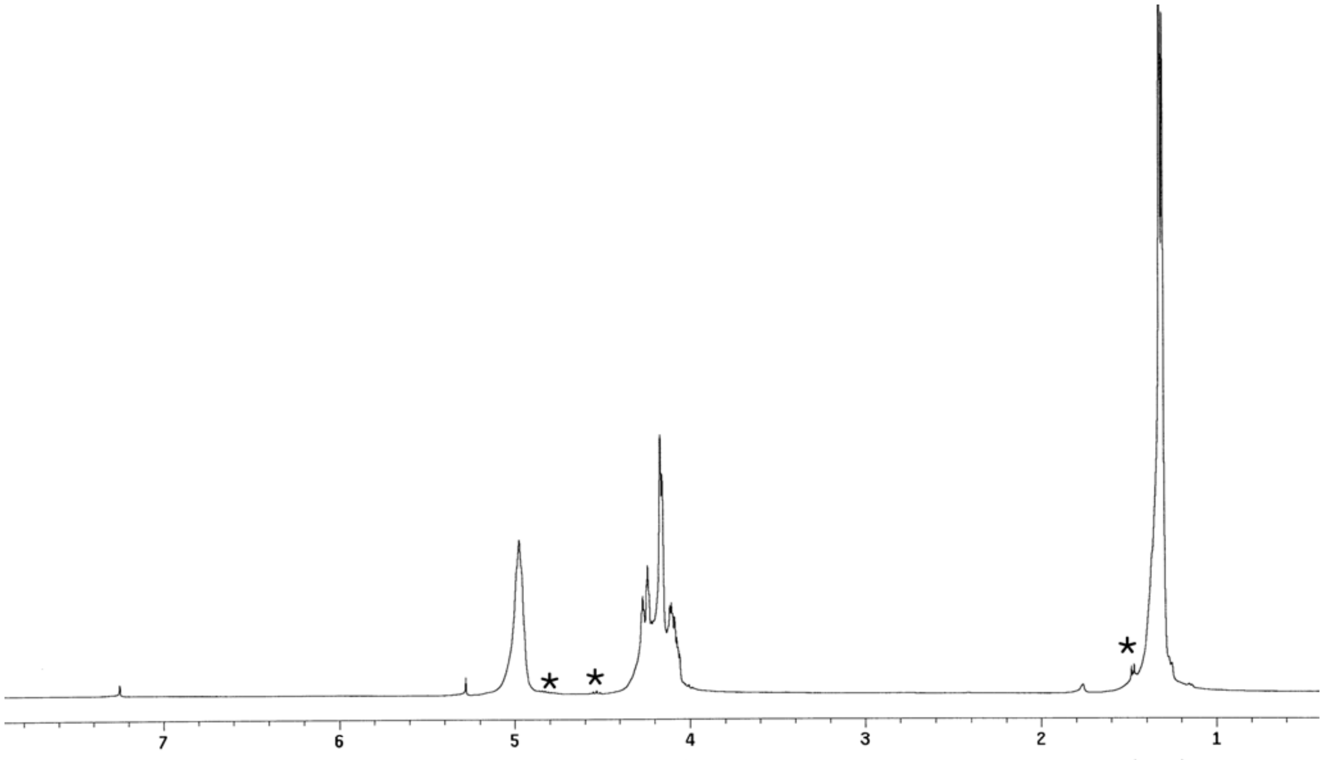
<The ^{1}H NMR spectrum (dmso-d$_6$, 38^{o}C) of the dihydroxylato complex prepared form **8** (X = BF$_4$)>


OH
X
NBu3
Bu3N
X-
N
Co
O
OH
X = BF4
MC
9
8
7
6
5
4
3
2
1
-0
-1
ppm

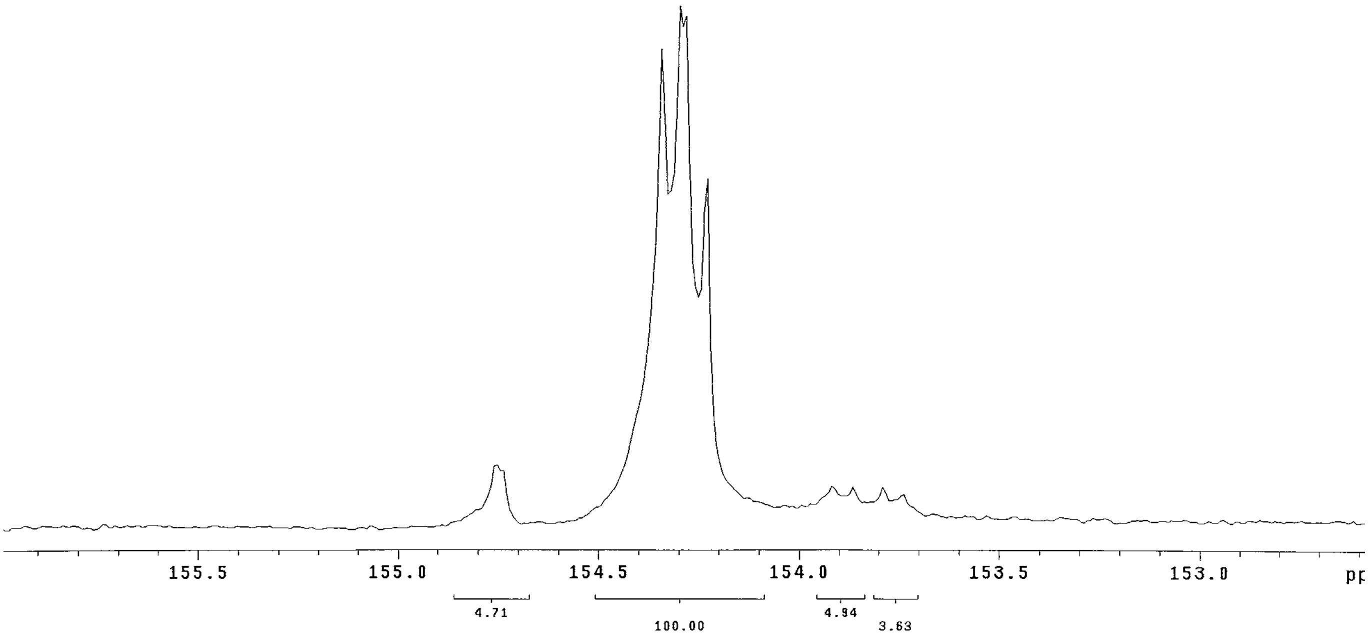
<The ^{1}H NMR spectrum ($CDCl_3$) of an aliquot of the polymerization solution (entry 1 in Table 2) >
Signals marked with asterisks are the cyclic carbonate signals, and large signals at 2-3 ppm are the monomer signals.



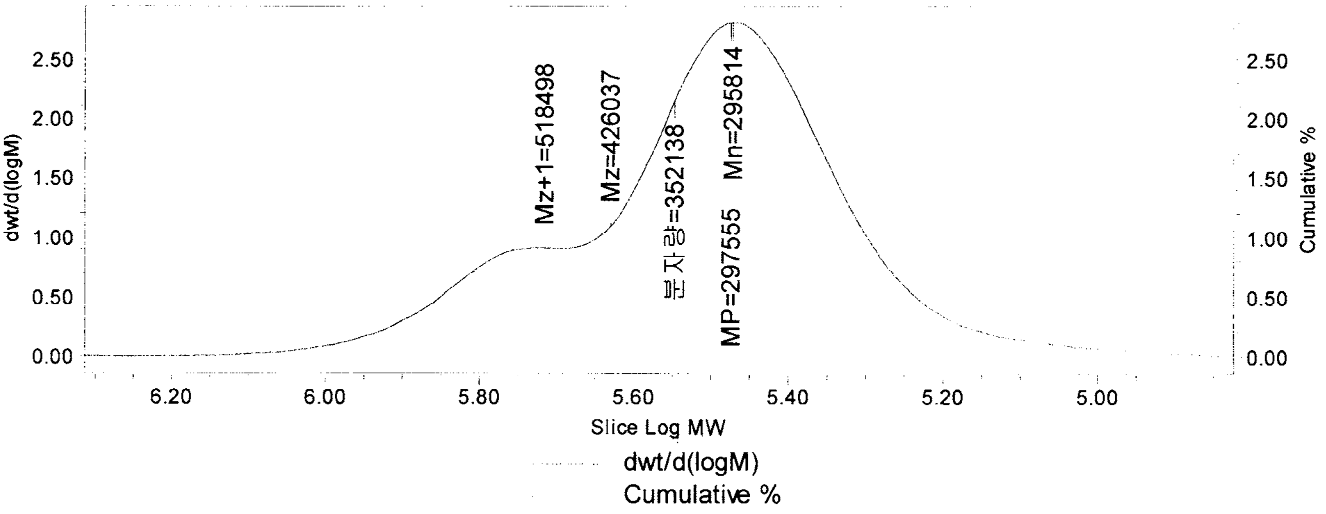
<The ^{1}H NMR spectrum ($CDCl_3$) of the isolated polymer (1st run in Table 2) >
Signals marked with asterisks are the cyclic carbonate signals.



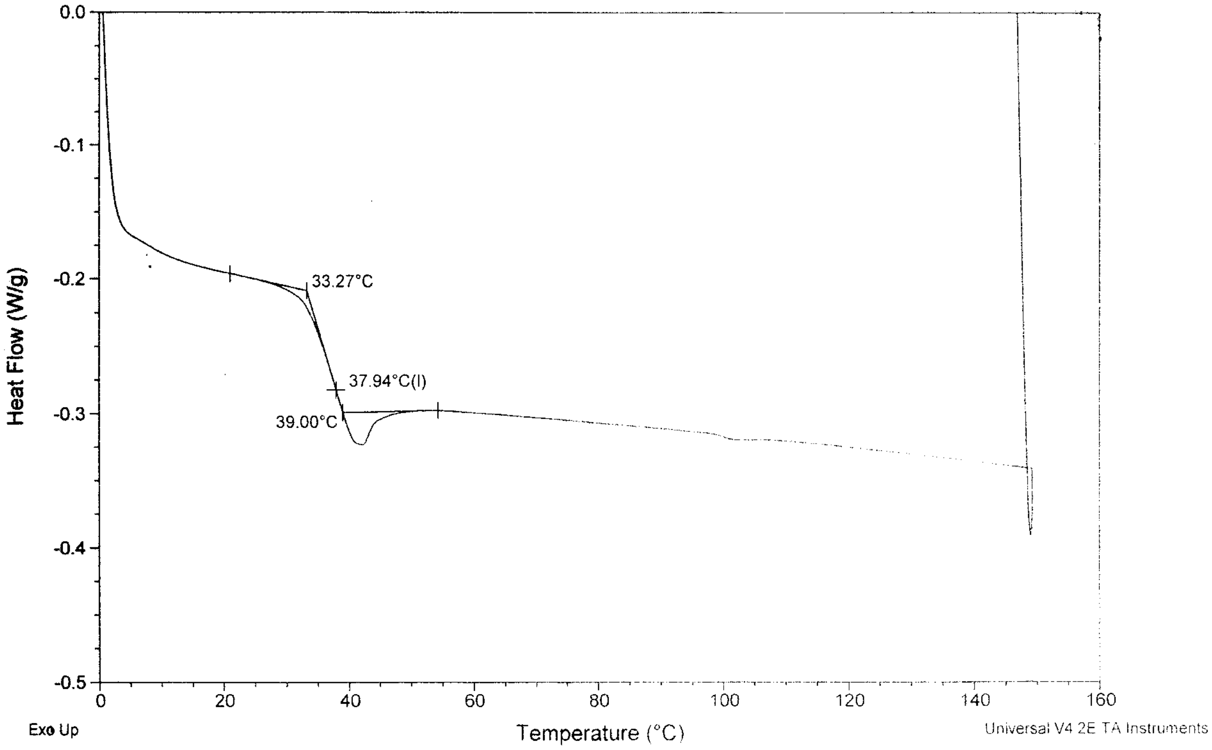
<The ^{13}C NMR spectrum (CDCl$_3$) of the isolated polymer (1st run in Table 2) >


155.5
155.0
154.5
154.0
153.5
153.0
pp
4.71
100.00
4.94
3.63

<The GPC curve of the isolated polymer (1st run in Table 2) >

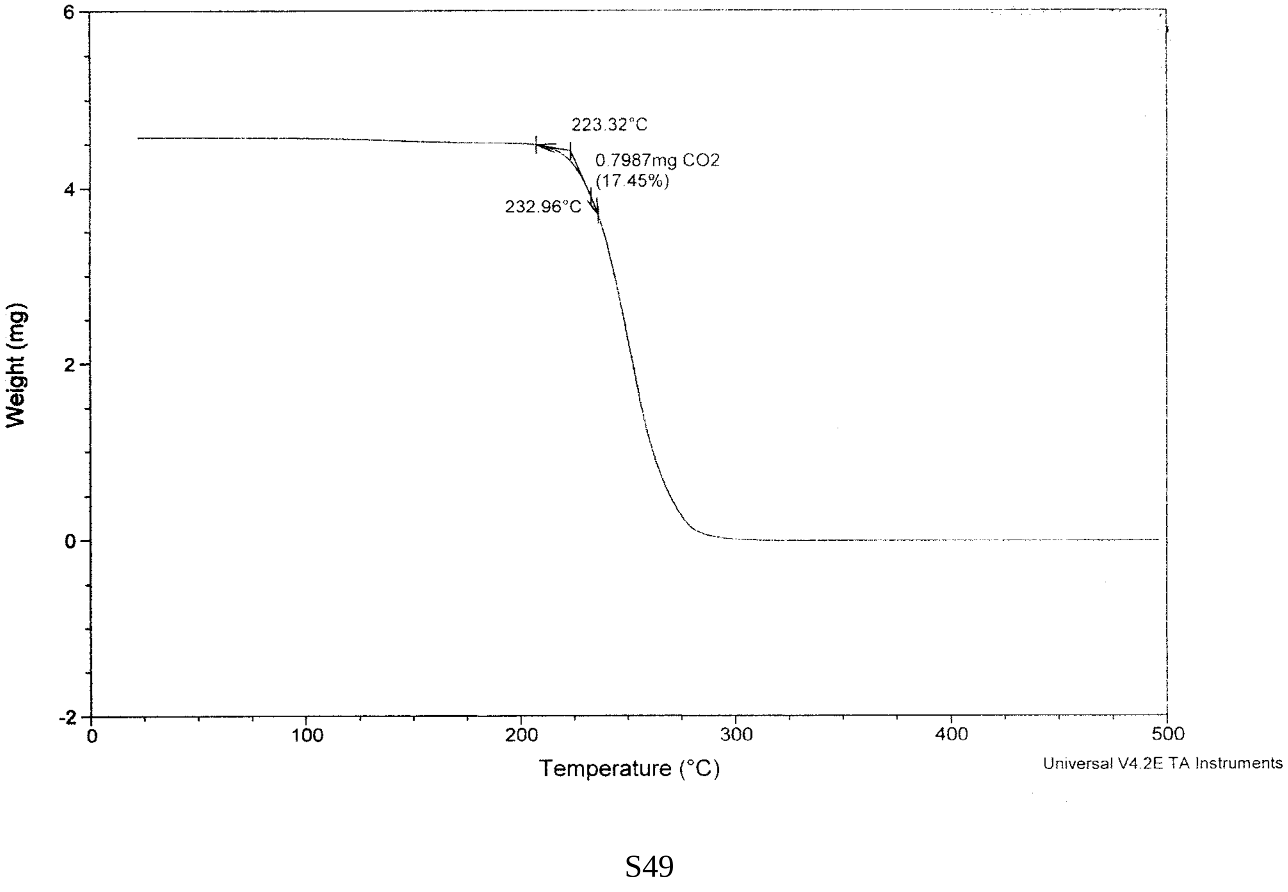

2.50
2.00
1.50
1.00
0.50
0.00
dwt/d(logM)
Cumulative %
Mz+1=518498
Mz=426037
분자량=352138
MP=297555
Mn=295814
6.20
6.00
5.80
5.60
5.40
5.20
5.00
Slice Log MW
dwt/d(logM)
Cumulative %

<The DSC curve of the high molecular-weight polymer (M_n, 296000) (1st run in Table 2) >



0.0
-0.1
-0.2
-0.3
-0.4
-0.5
Heat Flow (W/g)
33.27°C
37.94°C(I)
39.00°C
0
20
40
60
80
100
120
140
160
Exo Up
Temperature (°C)
Universal V4.2E TA Instruments

<The TGA curve of the high molecular-weight polymer (M_n, 296000 (1st run in Table 2) >



6
4
2
0
-2
Weight (mg)
223.32°C
0.7987mg CO2
(17.45%)
232.96°C
0
100
200
300
400
500
Temperature (°C)
Universal V4.2E TA Instruments